



Instituto de Química da UNICAMP

Eletroquímica

Candidato: Raphael Nagao

Estrutura da Aula

A) Termodinâmica eletroquímica

- A1) Potencial e afinidade eletroquímica;
- A2) Produção de entropia e Lei de Ohm;
- A3) Força eletromotriz e equação de Nernst;
- A4) Natureza dos potenciais;
- A5) Teoria de Debye-Hückel;
- A6) Curvas eletrocílicas;
- A7) Modelos da dupla camada elétrica;

B) Pontos importantes da aula

Bibliografia

A) Livros textos

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2. KONDEPUDI, D.; PRIGOGINE, I. **Modern Thermodynamics: From Heat Engines to Dissipative Structures.** Chichester: John Wiley & Sons, 1998.

B) Livros complementares

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C) Livros auxiliares

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A) Termodinâmica eletroquímica

A1) Potencial e afinidade eletroquímica

Espécies carregadas sob um campo elétrico possuem uma componente energética adicional ao potencial químico. Considerando o transporte dessas espécies em duas fases,

$$-dN_{1k} = dN_{2k} = d\xi_k$$

Pela conservação de energia,

$$dU = TdS - PdV + \sum_k \mu_{1k} dN_{1k} + \sum_k z_k F \phi_1 dN_{1k} + \sum_k \mu_{2k} dN_{2k} + \sum_k z_k F \phi_2 dN_{2k}$$

Incluindo a extensão da reação,

$$dU = TdS - PdV + \sum_k \mu_{1k} (-d\xi_k) + \sum_k z_k F \phi_1 (-d\xi_k) + \sum_k \mu_{2k} (d\xi_k) + \sum_k z_k F \phi_2 (d\xi_k)$$

Pode-se escrever,

$$TdS = dU + PdV + \sum_k \mu_{1k} d\xi_k + \sum_k z_k F \phi_1 d\xi_k - \sum_k \mu_{2k} d\xi_k - \sum_k z_k F \phi_2 d\xi_k$$

$$TdS = dU + PdV - \sum_k [(\mu_{2k} + z_k F \phi_2) - (\mu_{1k} + z_k F \phi_1)] d\xi_k$$

Portanto, definimos:

$$\tilde{\mu}_k = \mu_k + z_k F \phi$$

$$\tilde{A}_k = \sum_k \tilde{\mu}_k v_k$$

Reescrevendo,

$$TdS = dU + PdV + \sum_k \tilde{A}_k d\xi_k \quad \text{em que, } \tilde{A}_k = (\mu_{1k} + z_k F \phi_1) - (\mu_{2k} + z_k F \phi_2)$$

Pode-se escrever,

$$T(d_e S + d_i S) = (Td_e S - PdV) + PdV + \sum_k \tilde{A}_k d\xi_k \iff d_i S = \sum_k \frac{\tilde{A}_k}{T} d\xi_k$$

No estado de equilíbrio,

$$\tilde{A}_k = 0 \iff (\mu_{1k} + z_k F \phi_1) - (\mu_{2k} + z_k F \phi_2) = 0$$

Isolando,

$$(\mu_{1k} - \mu_{2k}) + z_k F(\phi_1 - \phi_2) = 0 \iff (\mu_{1k} - \mu_{2k}) = z_k F(\phi_2 - \phi_1)$$

Finalmente,

$$-(\mu_{2k} - \mu_{1k}) = z_k F(\phi_2 - \phi_1) \iff \Delta\phi = -\frac{\Delta\mu_k}{z_k F}$$

Como ϕ depende da distância,

$$\tilde{A}_k = \tilde{\mu}_k(x) - \tilde{\mu}_k(x + \delta) = \tilde{\mu}_k(x) - \left[\tilde{\mu}_k(x) + \left(\frac{\partial \tilde{\mu}_k(x)}{\partial x} \right) \delta \right] = -\left(\frac{\partial \tilde{\mu}_k}{\partial x} \right) \delta$$

Lembrando que,

$$\frac{d_i S}{dt} = \sum_k \frac{\tilde{A}_k}{T} \frac{d\xi_k}{dt} \Rightarrow \frac{d_i [s(x)\delta]}{dt} = \sum_k \frac{1}{T} \left[-\left(\frac{\partial \tilde{\mu}_k}{\partial x} \right) \delta \right] \frac{d\xi_k}{dt}$$

Podemos escrever a produção de entropia em termos do potencial eletroquímico,

$$\boxed{\frac{d_i s(x)}{dt} = - \sum_k \frac{1}{T} \left(\frac{\partial \tilde{\mu}_k}{\partial x} \right) J_{N_k}}$$

A2) Produção de entropia e Lei de Ohm

Abrindo a expressão,

$$\frac{\partial \tilde{\mu}_e}{\partial x} = \frac{\partial}{\partial x} (\mu_k + z_k F \phi) = -eF \frac{\partial \phi}{\partial x} \quad \text{em que, } z_k = -e$$

Lembrando que, $E_c = -\frac{\partial \phi}{\partial x}$; $I = -eFJ_e$; Portanto, obtemos: $\frac{\partial \tilde{\mu}_e}{\partial x} = eFE_c$

Logo,

$$\frac{d_i s(x)}{dt} = -\frac{1}{T} (eFE_c) \left(-\frac{I}{eF} \right) \Leftrightarrow \frac{d_i s(x)}{dt} = \frac{E_c I}{T}$$

Integrando sobre o comprimento,

$$\int_0^L \frac{d_i s(x)}{dt} dx = \int_0^L \frac{E_c I}{T} dx \quad \Rightarrow \quad \frac{d_i S}{dt} = \frac{EI}{T} = \frac{1}{T} \frac{dQ}{dt}$$

Por fim, tem-se:

$$I = L_e \frac{E}{T} \quad \text{em que, } L_e = \frac{T}{R} \quad \text{Logo, } \boxed{I = \frac{E}{R}}$$

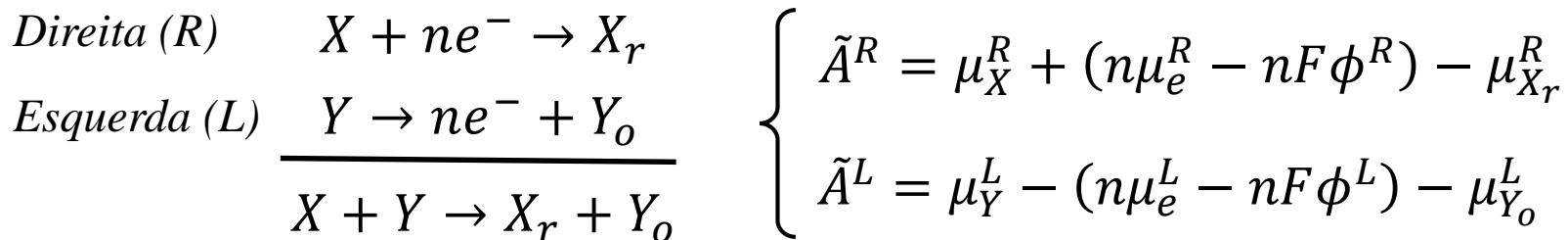
A3) Força eletromotriz e equação de Nernst

Lembrando das relações: $\frac{d_i S}{dt} = \sum_k \frac{\tilde{A}_k}{T} \frac{d\xi_k}{dt}; \quad I = nF \frac{d\xi_k}{dt}$

Pode-se escrever,

$$\frac{d_i S}{dt} = \frac{\tilde{A}_k}{T} \frac{I}{nF} \quad \Rightarrow \quad \frac{EI}{T} = \frac{\tilde{A}_k}{T} \frac{I}{nF} \quad \Leftrightarrow \quad \boxed{E = \frac{\tilde{A}_k}{nF}}$$

As afinidades das meias-reações,



A afinidade da reação global é dada por,

$$\tilde{A} = \tilde{A}^R + \tilde{A}^L = (\mu_X^R + \mu_Y^L - \mu_{X_r}^R - \mu_{Y_o}^L) + n(\mu_e^R - \mu_e^L) - nF(\phi^R - \phi^L)$$

No estado do equilíbrio, $\mu_e^R = \mu_e^L$, já que, $\tilde{A}_k = 0$

$$E = \frac{\tilde{A}_k}{nF} = \frac{(\mu_X^R + \mu_Y^L - \mu_{X_r}^R - \mu_{Y_o}^L)}{nF} - (\phi^R - \phi^L)$$

Definimos a força eletromotriz,

$$\frac{(\mu_X^R + \mu_Y^L - \mu_{X_r}^R - \mu_{Y_o}^L)}{nF} = (\phi^R - \phi^L) \equiv E_{emf}$$

Se há o fluxo de corrente, $\tilde{A}_k \neq 0$

$$\frac{(\mu_X^{o,R} + RT \ln a_X^R) + (\mu_Y^{o,L} + RT \ln a_Y^L) - (\mu_{X_r}^{o,R} + RT \ln a_{X_r}^R) - (\mu_{Y_o}^{o,L} + RT \ln a_{Y_o}^L)}{nF} = \Delta\phi = E$$

Pode-se escrever,

$$E = \frac{(\mu_X^{o,R} + \mu_Y^{o,L} - \mu_{X_r}^{o,R} - \mu_{Y_o}^{o,L})}{nF} + \frac{RT}{nF} \ln \left(\frac{a_X^R a_Y^L}{a_{X_r}^R a_{Y_o}^L} \right)$$

Equação de Nernst

$$E = E^o - \frac{RT}{nF} \ln \left(\prod_k a_k^{\nu_k} \right)$$

$$\Delta\phi = \Delta\phi^o - \frac{RT}{nF} \ln \left(\prod_k a_k^{\nu_k} \right)$$

Relembrando da expressão de equilíbrio,

$$e^{-\frac{\Delta G^o}{RT}} = \prod_k a_k^{v_k} \equiv K \Leftrightarrow -\frac{\Delta G^o}{RT} = \ln \left(\prod_k a_k^{v_k} \right)$$

Pode-se escrever,

$$0 = E^o - \frac{RT}{nF} \left(-\frac{\Delta G^o}{RT} \right) \Leftrightarrow \boxed{\Delta G^o = -nFE^o}$$

Assim podemos calcular a entropia,

$$\Delta S^o = - \left(\frac{\partial \Delta G^o}{\partial T} \right)_P \Rightarrow \boxed{\Delta S^o = nF \left(\frac{\partial E^o}{\partial T} \right)_P}$$

E a entalpia, pela relação,

$$\Delta H^o = \Delta G^o + T\Delta S^o = -nFE^o + nFT \left(\frac{\partial E^o}{\partial T} \right)_P$$

Finalmente,

$$\boxed{\Delta H^o = nF \left[T \left(\frac{\partial E^o}{\partial T} \right)_P - E^o \right]}$$

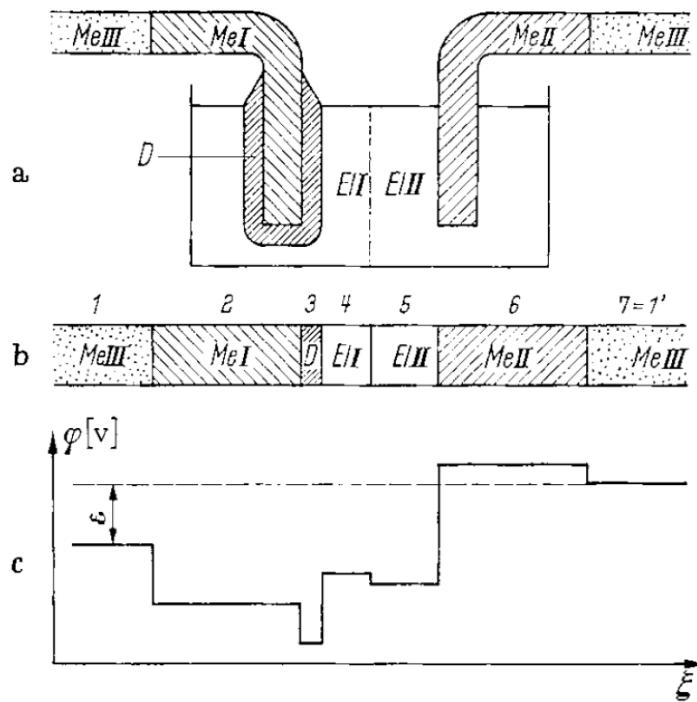


FIG. 2. Schematic potential diagram in a complicated galvanic cell. ω = cell voltage. Magnitudes and signs of potential changes are taken arbitrarily.

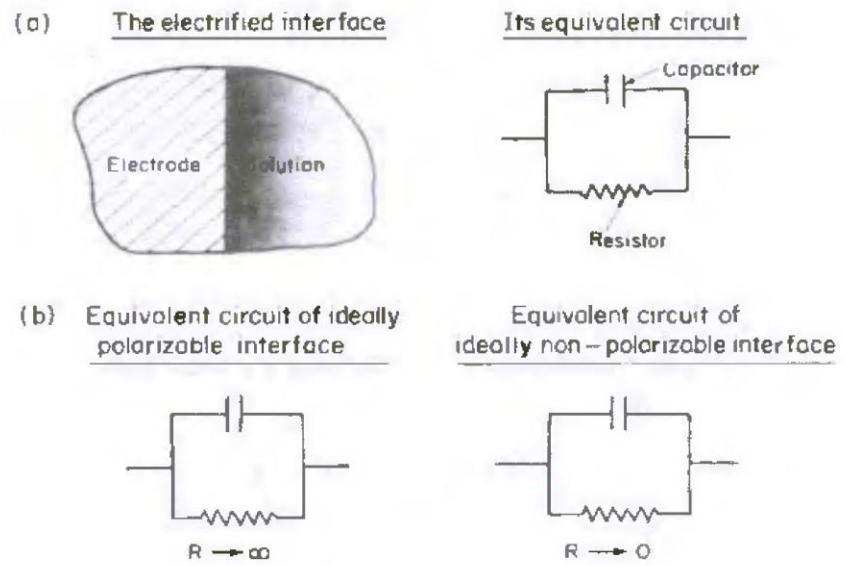
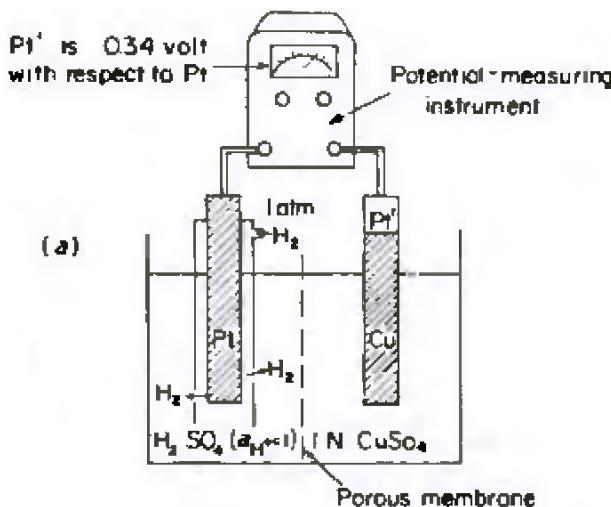


Fig. 6.33. (a) The equivalent circuit for an electrified interface is a capacitor and resistor connected in parallel. (b) In the equivalent circuit for an ideally polarizable interface, the resistance tends to infinity, and for a nonpolarizable interface, the resistance tends to zero.

A4) Natureza do potencial do eletrodo (E)



Pela segunda Lei de Kirchhoff,

$$\Delta\phi(Pt'|Cu) + \Delta\phi(Cu|S) + \Delta\phi^o(S|Pt) + \Delta\phi(Pt|Pt') = 0$$

$$\Delta\phi(Pt'|Cu) + \Delta\phi(Cu|S) + \Delta\phi^o(S|Pt) - \Delta\phi(Pt'|Pt) = 0$$

$$\Delta\phi(Pt'|Cu) + \Delta\phi(Cu|S) + \Delta\phi^o(S|Pt) = \Delta\phi(Pt'|Pt) \equiv E$$

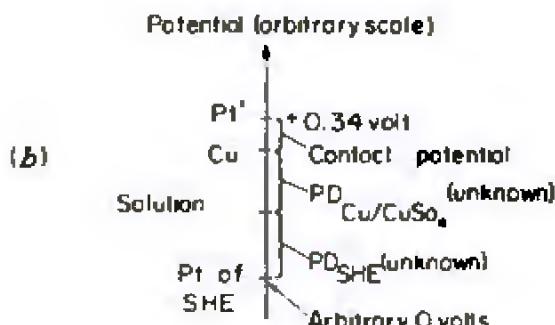
No estado padrão: $a_{Cu^{2+}} = 1$

$$\Delta\phi(Pt'|Cu) + \Delta\phi^o(Cu|S) + \Delta\phi^o(S|Pt) = \Delta\phi(Pt'|Pt) \equiv E^o$$

Pode-se escrever,

$$E - E^o = \Delta\phi(Cu|S) - \Delta\phi^o(Cu|S) = -\frac{RT}{nF} \ln\left(\frac{a_{Cu^{2+}}}{a_{Cu}}\right)$$

Finalmente, $E = E^o - \frac{RT}{nF} \ln a_{Cu^{2+}}$

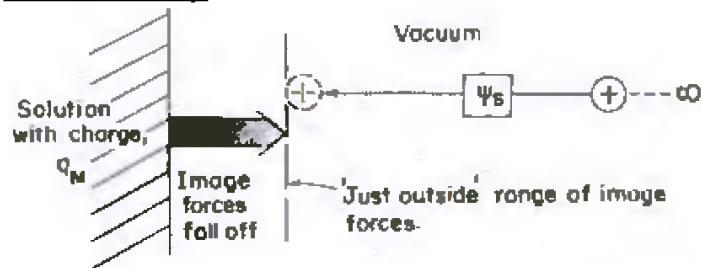


A utilização de um eletrodo não-polarizável nos fornece a possibilidade de estudar a interface de interesse,

$$\delta E = \delta\Delta\phi(Pt'|Cu) + \delta\Delta\phi(Cu|S) + \delta\Delta\phi^o(S|Pt) \Rightarrow \boxed{\delta E \approx \delta\Delta\phi(Cu|S)}$$

A4) Natureza do potencial do Galvani ϕ

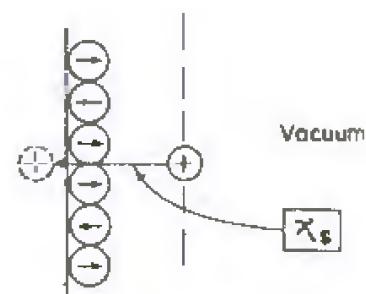
$$\phi = \psi + \chi \Rightarrow \Delta\phi(M|S) = \Delta\psi(M|S) + \Delta\chi(M|S)$$



$$\psi = - \int_{\infty}^r \frac{1}{4\pi\epsilon_0} \frac{|q|}{4r^2} dr = - \frac{1}{4\pi\epsilon_0} \frac{|q|}{4r}$$

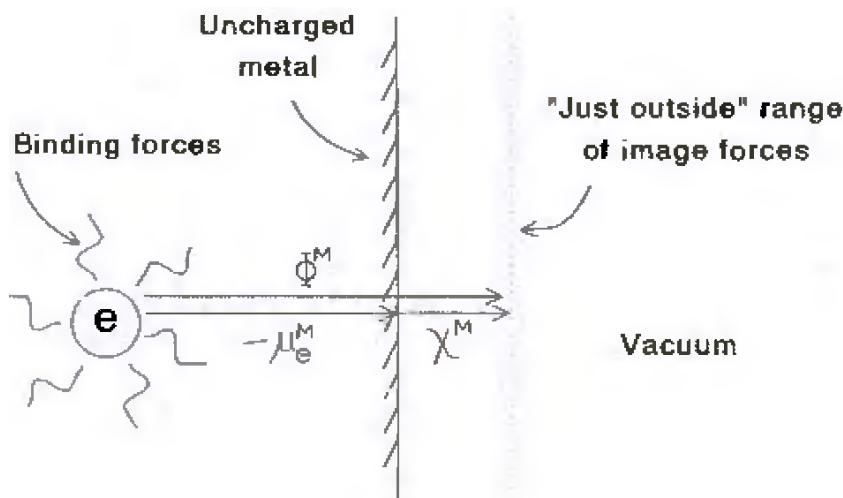
$$\Delta\psi(M|S) = \psi^M - \psi^S$$

(potencial de Volta)



$$\Delta\chi(M|S) = \chi^M - \chi^S$$

(potencial de dipolo)



$$\Phi^M = -\mu_e^M - zF\chi^M$$

(função trabalho)

$$\Phi^M = -\mu_e^M + F\chi^M$$

A5) Teoria de Debye-Hückel

Energia de interação entre íon e nuvem iônica,

$$\Delta\mu_{i-I} = N_A W = N_A \frac{Z_i e_0}{2} \psi$$

Considera-se uma distribuição de Poisson,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) = - \frac{4\pi}{\epsilon} \rho_r$$

A densidade de carga pode se escrita como,

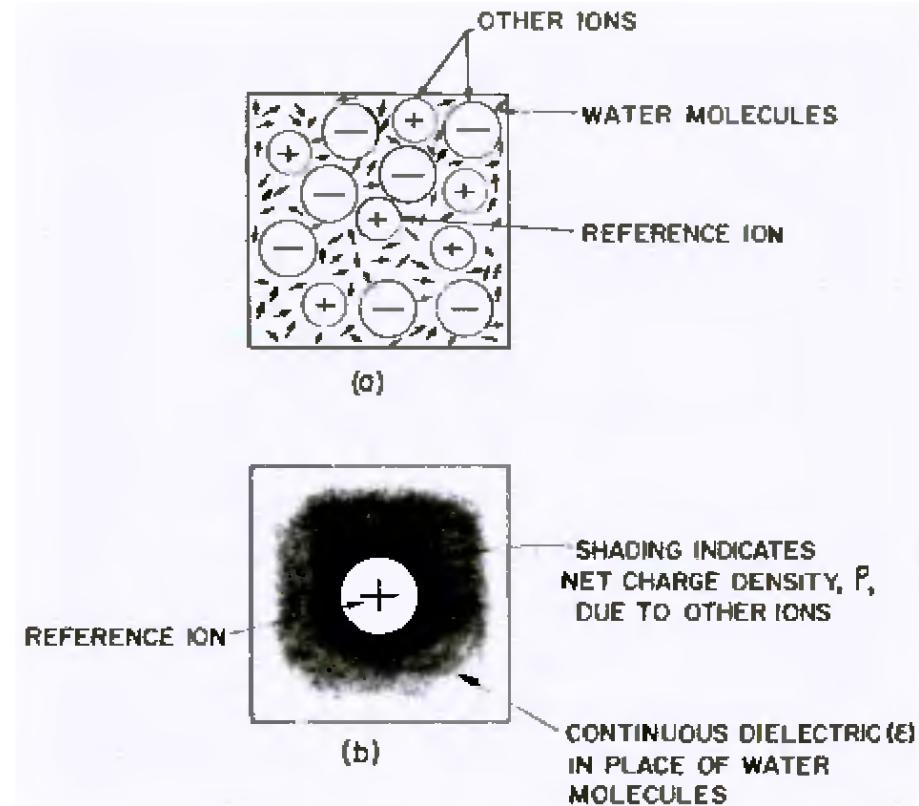
$$\rho_r = \sum_i n_i Z_i e_0$$

Os íons seguem uma distribuição de Boltzmann: $n_i = n_i^0 e^{-\frac{U}{k_B T}}$ em que, $U = z_i e_0 \psi_r$

$$n_i = n_i^0 e^{-\frac{z_i e_0 \psi_r}{k_B T}} \quad \Rightarrow \quad \rho_r = \sum_i n_i^0 Z_i e_0 e^{-\frac{z_i e_0 \psi_r}{k_B T}}$$

Expandindo em uma série de Taylor,

$$e^{-\frac{z_i e_0 \psi_r}{k_B T}} = 1 - \frac{z_i e_0 \psi_r}{k_B T} + \frac{1}{2} \left(\frac{z_i e_0 \psi_r}{k_B T} \right)^2 + \dots \quad \text{para, } z_i e_0 \psi_r \ll k_B T$$



Pode-se escrever,

$$\rho_r = \sum_i n_i^0 z_i e_0 \left(1 - \frac{z_i e_0 \psi_r}{k_B T} \right) \Leftrightarrow \rho_r = \sum_i n_i^0 z_i e_0 - \sum_i \frac{n_i^0 z_i^2 e_0^2 \psi_r}{k_B T}$$

Gibbs-Duhem,

$$\sum_i n_i^0 z_i e_0 = 0 \Rightarrow \rho_r = - \sum_i \frac{n_i^0 z_i^2 e_0^2 \psi_r}{k_B T}$$

Relembrando,

$$\rho_r = - \frac{\varepsilon}{4\pi r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right)$$

Assim, temos,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) = \left(\frac{4\pi}{\varepsilon k_B T} \sum_i n_i^0 z_i^2 e_0^2 \right) \psi_r$$

$$em que, \kappa^2 = \frac{4\pi}{\varepsilon k_B T} \sum_i n_i^0 z_i^2 e_0^2$$

Logo,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) = \kappa^2 \psi_r \quad para, \quad \psi_r = \frac{u}{r} \Rightarrow \frac{d\psi_r}{dr} = \frac{d}{dr} \left(\frac{u}{r} \right) = -\frac{u}{r^2} + \frac{1}{r} \frac{du}{dr}$$

Pode-se escrever,

$$\frac{1}{r^2} \frac{d}{dr} \left[r^2 \left(-\frac{u}{r^2} + \frac{1}{r} \frac{du}{dr} \right) \right] = \frac{1}{r^2} \left(-\frac{du}{dr} + r \frac{d^2 u}{dr^2} + \frac{du}{dr} \right) = \frac{1}{r} \frac{d^2 u}{dr^2}$$

Temos,

$$\frac{1}{r} \frac{d^2 u}{dr^2} = \kappa^2 \frac{u}{r} \quad \text{Sabendo-se que: } \frac{d}{dr} e^{\pm \kappa r} = \pm \kappa e^{\pm \kappa r} \quad \text{e} \quad \frac{d^2}{dr^2} e^{\pm \kappa r} = \kappa^2 e^{\pm \kappa r}$$

Pode-se escrever,

$$u = A e^{-\kappa r} + B e^{+\kappa r} \Rightarrow \psi_r = A \frac{e^{-\kappa r}}{r} + B \frac{e^{+\kappa r}}{r}$$

Aplicando a condição de contorno, $\begin{array}{l} r \rightarrow \infty \\ \psi_r \rightarrow 0 \end{array}$ $\psi_r = A \frac{e^{-\kappa r}}{r}; \quad B = 0$

Relembrando das expressões,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) = \kappa^2 \psi_r \quad \text{e} \quad \rho_r = -\frac{\epsilon}{4\pi} \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right)$$

Substituindo,

$$\rho_r = -\frac{\epsilon}{4\pi} \kappa^2 A \frac{e^{-\kappa r}}{r} \quad \text{em que, } dq = \rho_r 4\pi r^2 dr \Rightarrow dq = -A \kappa^2 \epsilon e^{-\kappa r} r dr$$

Integrando,

$$\int_a^\infty dq = -A \kappa^2 \epsilon \int_a^\infty e^{-\kappa r} r dr \Leftrightarrow -z_i e_0 = -A \epsilon \int_a^\infty e^{-\kappa r} (\kappa r) d(\kappa r)$$

Ainda na integração,

$$-A\varepsilon \int_a^{\infty} e^{-\kappa r} (\kappa r) d(\kappa r) = (\kappa r) \left(-e^{-\kappa r} \Big|_a^{\infty} \right) + \int_a^{\infty} e^{-\kappa r} d(\kappa r)$$

Obtemos,

$$-z_i e_0 = -A\varepsilon \left(\kappa a e^{-\kappa a} - e^{-\kappa r} \Big|_a^{\infty} \right) \Leftrightarrow -z_i e_0 = -A\varepsilon e^{-\kappa a} (1 + \kappa a)$$

Isolando A, temos,

$$A = \frac{z_i e_0}{\varepsilon} \frac{e^{\kappa a}}{(1 + \kappa a)}$$

Substituindo,

$$\psi_r = A \frac{e^{-\kappa r}}{r} \Rightarrow \psi_r = \frac{z_i e_0}{\varepsilon} \frac{e^{\kappa a}}{(1 + \kappa a)} \frac{e^{-\kappa r}}{r}$$

Sabendo-se que,

$$\psi_r = \psi_{ion} + \psi_{cloud} \Rightarrow \psi_{cloud} = \psi_r - \psi_{ion} = \frac{z_i e_0}{\varepsilon} \frac{e^{\kappa a}}{(1 + \kappa a)} \frac{e^{-\kappa r}}{r} - \frac{z_i e_0}{\varepsilon r}$$

Finalmente, $\psi_{cloud} = \frac{z_i e_0}{\varepsilon r} \left[\frac{e^{-\kappa(r-a)}}{(1 + \kappa a)} - 1 \right]$ porém, $e^{\pm x}(x \rightarrow 0) \approx 1 \pm x$

Logo,

$$\frac{e^{-\kappa(r-a)}}{(1 + \kappa a)} - 1 = \frac{e^{-\kappa(r-a)} - (1 + \kappa a)}{(1 + \kappa a)} = \frac{1 - \kappa(r - a) - (1 + \kappa a)}{(1 + \kappa a)}$$

Continuando,

$$\frac{1 - \kappa(r - a) - (1 + \kappa a)}{(1 + \kappa a)} = -\frac{\kappa r}{(1 + \kappa a)} = -\frac{r}{\kappa^{-1}(1 + \kappa a)}$$

Pode-se escrever,

$$\psi_{cloud} = \frac{z_i e_0}{\varepsilon r} \left[-\frac{r}{\kappa^{-1}(1 + \kappa a)} \right] = -\frac{z_i e_0}{\varepsilon \kappa^{-1}(1 + \kappa a)}$$

Lembrando que,

$$\Delta \mu_{i-I} = N_A \frac{z_i e_0}{2} \psi$$

$$\psi = \psi_{cloud}(r = a)$$

$$\mu_k(\text{ideal}) = \mu_k^o(P, T) + RT \ln x_k$$

$$\mu_k(\text{real}) = \mu_k^o(P, T) + RT \ln x_k + RT \ln \gamma_k$$

$$\Delta \mu_{i-I} = RT \ln \gamma_k$$

Temos uma relação com o coeficiente de atividade,

$$RT \ln \gamma = N_A \frac{z_i e_0}{2} \psi_{cloud} \Leftrightarrow RT \ln \gamma = N_A \frac{z_i e_0}{2} \left[-\frac{z_i e_0}{\varepsilon \kappa^{-1}(1 + \kappa a)} \right]$$

Ou seja,

$$\ln \gamma = -\frac{N_A (z_i e_0)^2}{2 \varepsilon R T \kappa^{-1}} \frac{1}{(1 + \kappa a)}$$

Sabendo-se que,

$$\ln\gamma_{\pm} = \frac{1}{(v_+ + v_-)} (v_+ \ln\gamma_+ + v_- \ln\gamma_-) \quad \text{em que, } v = v_+ + v_-$$

Assim, temos,

$$\ln\gamma_+ = -\frac{N_A(z_+e_0)^2}{2\varepsilon RT\kappa^{-1}} \frac{1}{(1 + \kappa a)} \quad \ln\gamma_- = -\frac{N_A(z_-e_0)^2}{2\varepsilon RT\kappa^{-1}} \frac{1}{(1 + \kappa a)}$$

Substituindo,

$$\ln\gamma_{\pm} = -\frac{1}{v} \left[\frac{N_A e_0^2}{2\varepsilon RT\kappa^{-1}} \frac{(v_+ z_+^2 + v_- z_-^2)}{(1 + \kappa a)} \right]$$

Pode-se escrever,

$$v_+ z_+^2 + v_- z_-^2 = v_+ z_+ z_+ + v_- z_- z_- = v_+ z_+ z_- + v_- z_- z_+ = z_+ z_- v$$

Assim,

$$\ln\gamma_{\pm} = -\frac{1}{v} \left[\frac{N_A e_0^2}{2\varepsilon RT\kappa^{-1}} \frac{(z_+ z_- v)}{(1 + \kappa a)} \right] = -\frac{N_A (z_+ z_-) e_0^2}{2\varepsilon RT\kappa^{-1}} \frac{1}{(1 + \kappa a)}$$

Sabendo-se que,

$$\kappa^2 = \frac{4\pi}{\varepsilon k_B T} \sum_i n_i^0 z_i^2 e_0^2 \quad n_i^0 = \frac{c_i N_A}{1000} \quad I = \frac{1}{2} \sum_i c_i z_i^2$$

Substituindo,

$$\kappa^2 = \frac{4\pi}{\varepsilon k_B T} \sum_i n_i^0 z_i^2 e_0^2 = \frac{4\pi}{\varepsilon k_B T} \sum_i \left(\frac{c_i N_A}{1000} \right) z_i^2 e_0^2 = \frac{4\pi}{\varepsilon k_B T} \frac{N_A e_0^2}{1000} \sum_i c_i z_i^2$$

Pode-se escrever,

$$\kappa^2 = \frac{4\pi}{\varepsilon k_B T} \frac{e_0^2 N_A}{1000} 2I \Leftrightarrow \kappa = \left(\frac{8\pi N_A e_0^2}{1000 \varepsilon k_B T} \right)^{1/2} I^{1/2}$$

$$\kappa = BI^{1/2}; \quad B = \left(\frac{8\pi N_A e_0^2}{1000 \varepsilon k_B T} \right)^{1/2}$$

Logo,

$$\ln \gamma_{\pm} = - \frac{N_A (z_+ z_-) e_0^2}{2 \varepsilon R T} \frac{BI^{1/2}}{(1 + BI^{1/2} a)}$$

$$\log \gamma_{\pm} = - \frac{1}{2.303} \frac{N_A (z_+ z_-) e_0^2}{2 \varepsilon R T} \frac{BI^{1/2}}{(1 + BI^{1/2} a)} \quad \text{em que, } A = \frac{B}{2.303} \frac{N_A e_0^2}{2 \varepsilon R T}$$

$$\boxed{\log \gamma_{\pm} = - \frac{A(z_+ z_-) I^{1/2}}{(1 + BI^{1/2} a)}}$$

$$\boxed{\log \gamma_{\pm} = -A(z_+ z_-) I^{1/2}}$$

$$I \rightarrow 0$$

$$\log \gamma_{\pm} = -A(z_+ z_-) I^{1/2}$$

$$I \leq 0.01 \text{ mol kg}^{-1}$$

$$\log \gamma_{\pm} = -\frac{A(z_+ z_-) I^{1/2}}{(1 + BI^{1/2}a)}$$

Se o valor de a é conhecido,
 $I \leq 0.1 \text{ mol kg}^{-1}$

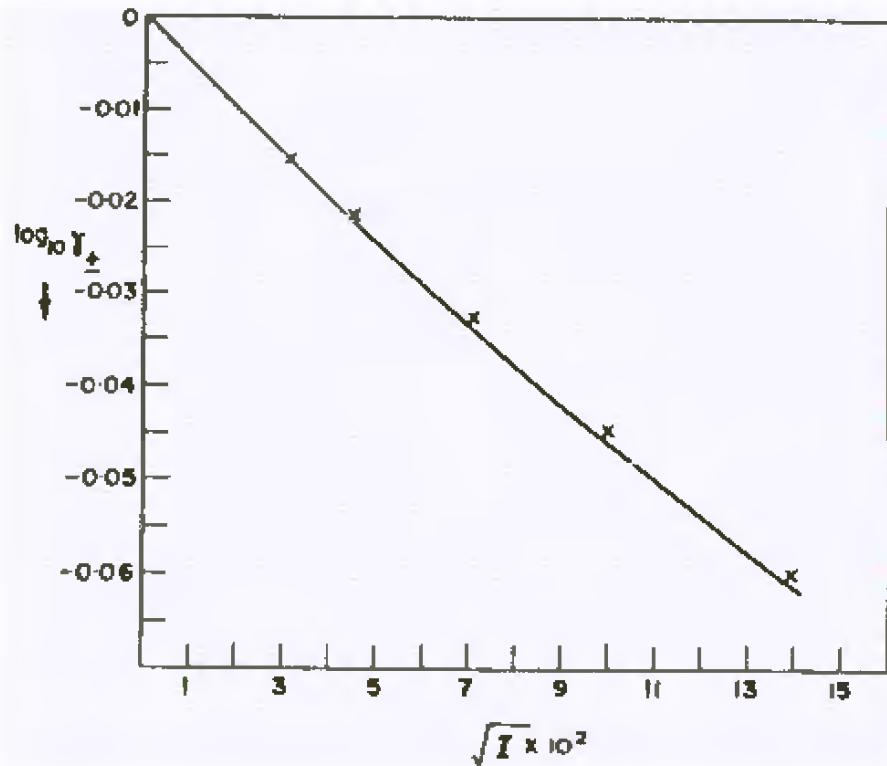


Fig. 3.34. Comparison of the experimental mean activity coefficients for sodium chloride with the theoretical $\log \gamma_{\pm}$ versus $I^{1/2}$ curve based on Eq. (3.126) with $a = 0.4 \text{ nm}$.

A6) Curvas eletrocapilares

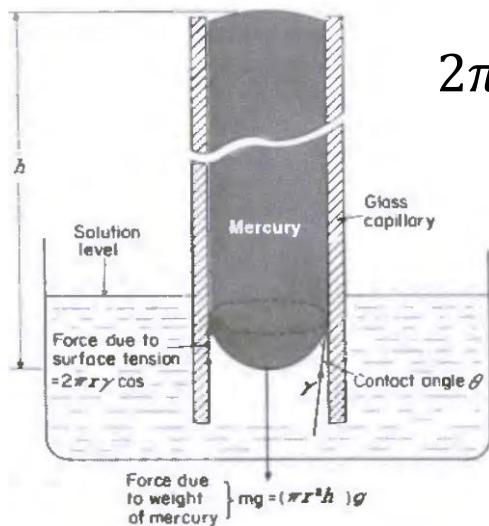
Pela 1^a e 2^a leis da Termodinâmica,

$$dU = TdS - PdV - \sigma dA - \Delta\phi(M|S)dq_M - \sum_i \mu_i dn_i$$

Portanto,

$$SdT - VdP - Ad\sigma - q_M d\Delta\phi(M|S) - \sum_i n_i d\mu_i = 0$$

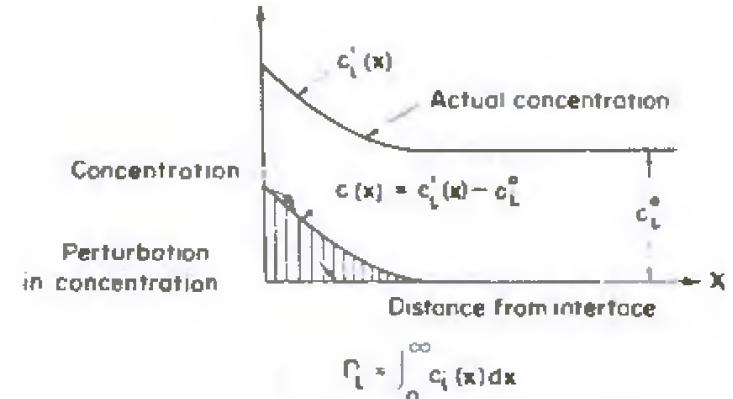
$$-Ad\sigma - q_M d\Delta\phi(M|S) - \sum_i n_i d\mu_i = 0 \Leftrightarrow d\sigma = -\frac{q_M}{A} d\Delta\phi(M|S) - \sum_i \frac{n_i}{A} d\mu_i$$



$$2\pi r \cdot \sigma \cos\theta = \pi r^2 h \rho g$$

$$\theta \approx 0$$

$$\sigma = \frac{rh\rho g}{2}$$



$$\Gamma_i = \int_0^\infty c_i(x) dx = \int_0^\infty (c_i'(x) - c_i^0) dx$$

Pode-se escrever,

$$\Gamma_i = \frac{1}{A} \int_0^\infty (c'_i(x) - c_i^0) dV = \frac{1}{A} \int_0^\infty (dn_i(x) - dn_i^0) = \frac{n_i}{A} - \frac{n_i^0}{A}$$

“ n_i número de mols das espécies i
na região da interfase”

“ n_i^0 número de mols das espécies i
sem a presença da dupla camada”

Logo,

$$d\sigma = -\frac{q_M}{A} d\Delta\phi(M|S) - \sum_i \left(\Gamma_i + \frac{n_i^0}{A} \right) d\mu_i \quad \text{em que, } \frac{n_i}{A} = \left(\Gamma_i + \frac{n_i^0}{A} \right)$$

Abrindo a expressão,

$$d\sigma = -\frac{q_M}{A} d\Delta\phi(M|S) - \sum_i \Gamma_i d\mu_i - \sum_i \frac{n_i^0}{A} d\mu_i \quad \text{em que, } \sum_i n_i^0 d\mu_i = 0$$

Assim, temos,

$$d\sigma = -q'_M d\Delta\phi(M|S) - \sum_i \Gamma_i d\mu_i$$

Em termos do potencial E ,

$$E = \Delta\phi(M|S) + \Delta\phi(S|R) + \Delta\phi^o(R|M') \Rightarrow dE = d\Delta\phi(M|S) + d\Delta\phi(S|R)$$

$$-d\Delta\phi(M|S) = -dE + d\Delta\phi(S|R)$$

Pode-se escrever,

$$d\sigma = -q'_M dE + q'_M d\Delta\phi(S|R) - \sum_i \Gamma_i d\mu_i$$

$$d\Delta\phi = -\frac{d\mu_j}{z_j F}$$

Finalmente, obtemos,

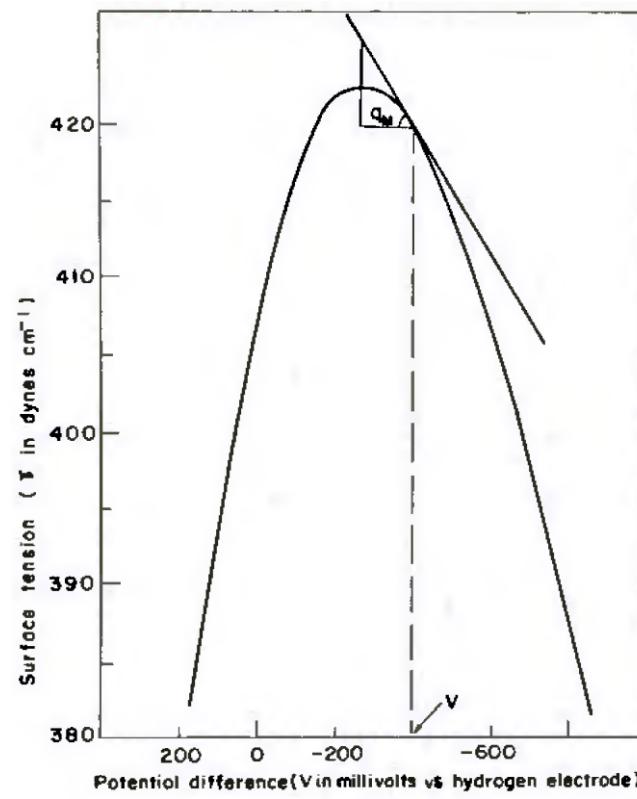
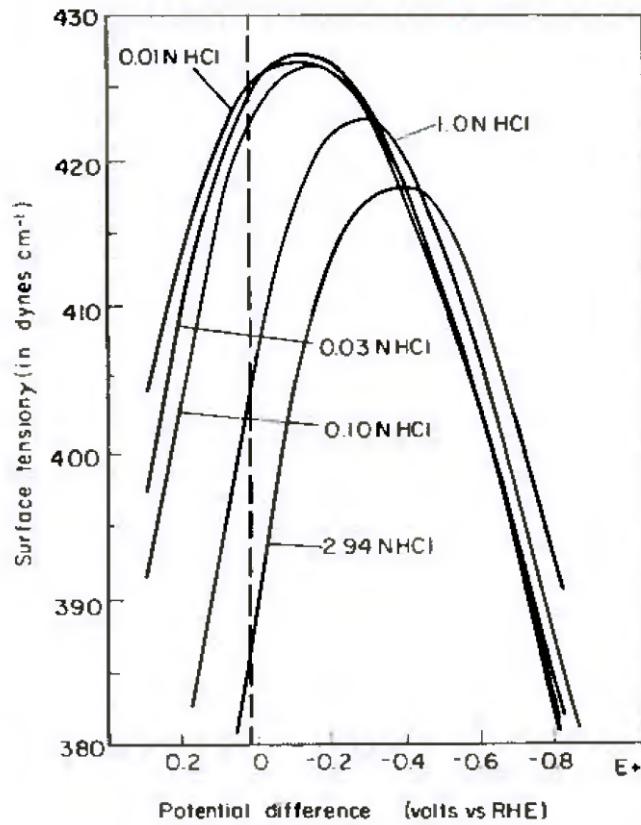
$$d\sigma = -q'_M dE - q'_M \frac{d\mu_j}{z_j F} - \sum_i \Gamma_i d\mu_i$$

Equação de Lippmann

$$\left(\frac{d\sigma}{dE} \right)_{a_{ij}} = -q'_M$$

$$\sum_i \Gamma_i d\mu_i = 0$$

$$d\mu_j = 0$$



Para E constante,

$$dE = 0 \Rightarrow d\sigma = -q_M \frac{d\mu_j}{z_j F} - \sum_i \Gamma_i d\mu_i \Leftrightarrow d\sigma = +q_M \frac{d\mu_-}{F} - \Gamma_+ d\mu_+ - \Gamma_- d\mu_-$$

Assim,

$$\begin{aligned} \mu &= \mu_+ + \mu_- \\ d\mu &= d\mu_+ + d\mu_- \end{aligned} \quad d\sigma = q_M \frac{d\mu_-}{F} - \Gamma_+ d\mu - \Gamma_+ d\mu_- - \Gamma_- d\mu_-$$

Escrevemos,

$$d\sigma = -\Gamma_+ d\mu + \left(\frac{q_M - F\Gamma_+ - F\Gamma_-}{F} \right) d\mu_- \quad \text{Pela eletroneutralidade:} \\ F \left(\frac{n_+^0}{A} \right) - F \left(\frac{n_-^0}{A} \right) = 0$$

Na presença da dupla camada,

$$q_M + F \left(\frac{n_+}{A} \right) - F \left(\frac{n_-}{A} \right) = 0 \Rightarrow q_M + F \left(\frac{n_+ - n_+^0}{A} \right) - F \left(\frac{n_- - n_-^0}{A} \right) = 0$$

Escrevermos, portanto,

$$q_M + F\Gamma_+ - F\Gamma_- = 0 \Rightarrow d\sigma = -\Gamma_+ d\mu \Leftrightarrow$$

$$-\Gamma_+ = \left(\frac{d\sigma}{d\mu} \right)_{E_-}$$

Finalmente,

$$\mu = \mu_+ + \mu_- = (\mu_+^0 + \mu_-^0) + (RT \ln a_+ + RT \ln a_-) = (\mu_+^0 + \mu_-^0) + RT \ln a_+ a_-$$

$$\mu = (\mu_+^0 + \mu_-^0) + 2RT \ln a_\pm$$

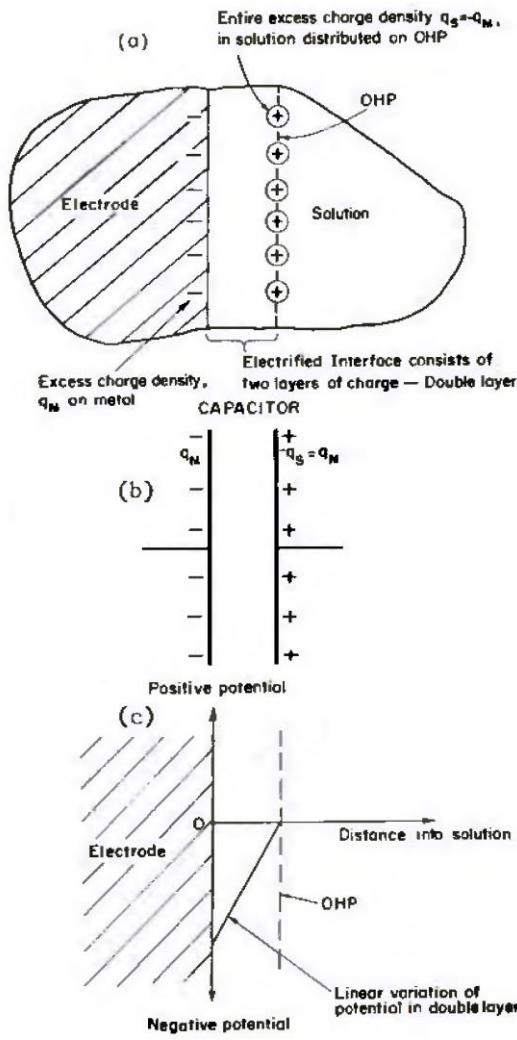
$$-\Gamma_+ = \frac{1}{2RT} \left(\frac{d\sigma}{d \ln a_\pm} \right)_{E_-}$$

$$d\mu = RT d \ln a_\pm^2$$

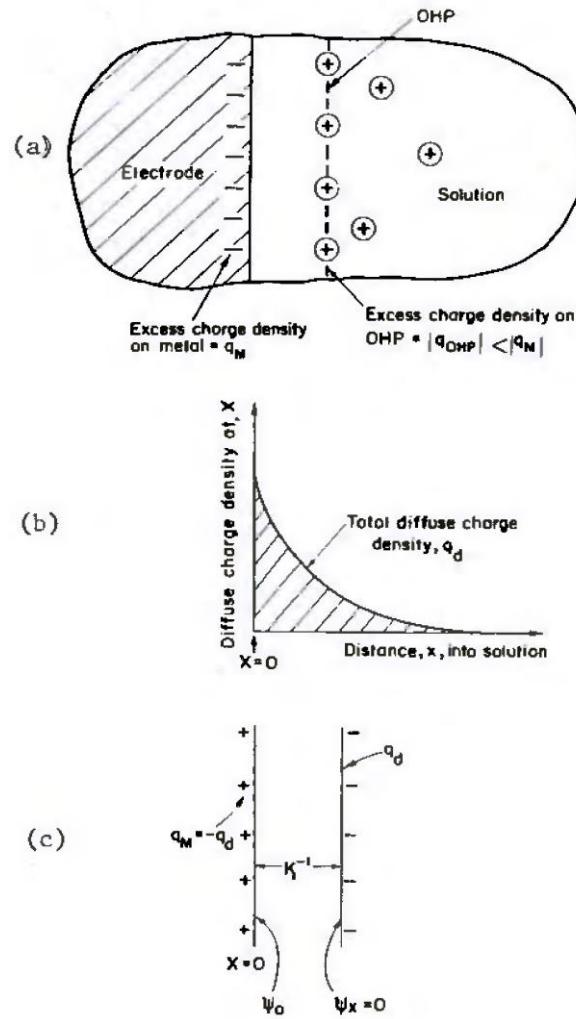
$$-\Gamma_- = \frac{1}{2RT} \left(\frac{d\sigma}{d \ln a_\pm} \right)_{E_+}$$

A7) Modelos da dupla camada elétrica

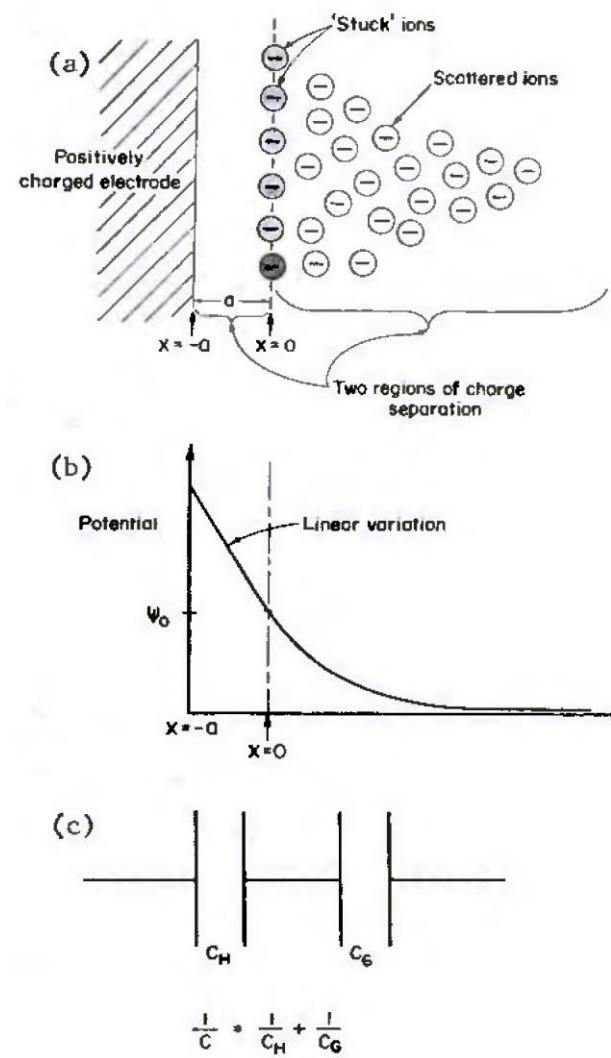
Helmholtz-Perrin



Gouy-Chapman



Stern-Grahame-Bockris



B) Pontos importantes da aula

- Potencial eletroquímico possui uma *contribuição elétrica* devido à presença de *acúmulo de carga sob um campo elétrico*;
- A *força eletromotriz* surge da condição de equilíbrio, e a *equação de Nernst* quando há fluxo de corrente;
- Podemos calcular o *coeficiente de atividade* por meio da *teoria de Debye-Hückel* (resolver uma equação do tipo Poisson-Boltzmann);
- A *estrutura da dupla camada* pode ser analisada em termos das *curvas eletrocapilares*;
- Modelos da dupla camada: *Helmholtz-Perrin*, *Gouy-Chapman*, *Stern-Grahame-Bockris*;