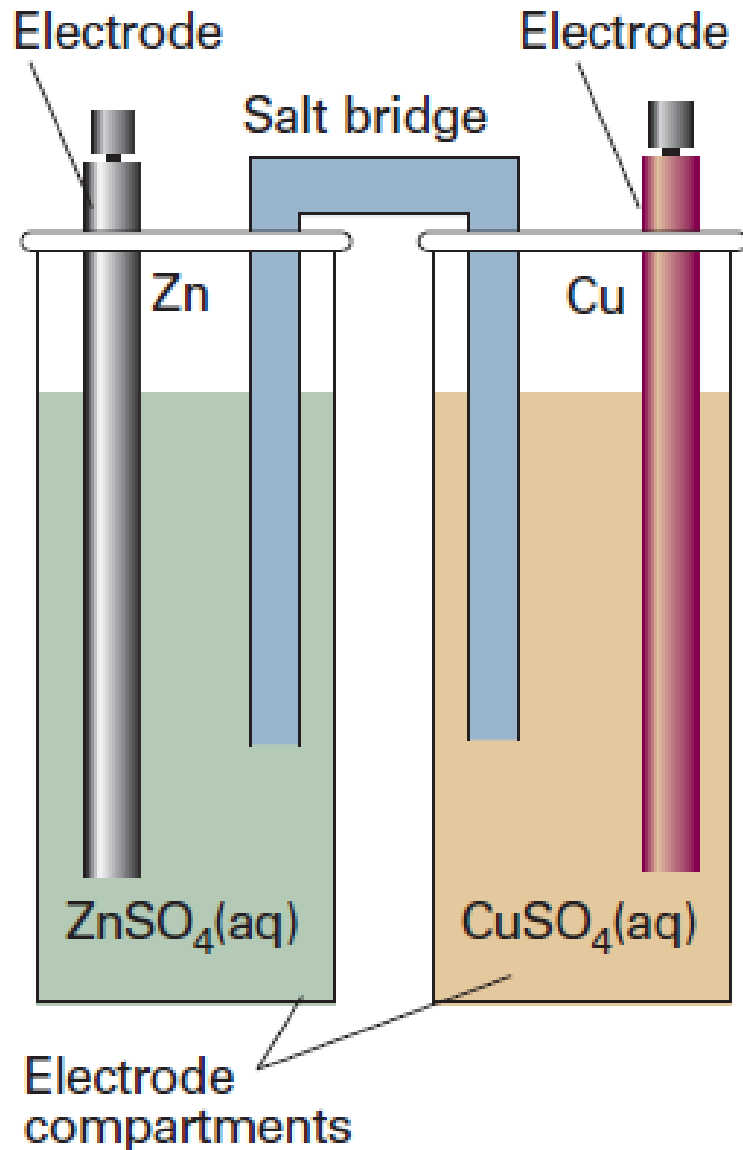


Universidade de São Paulo
Instituto de Química

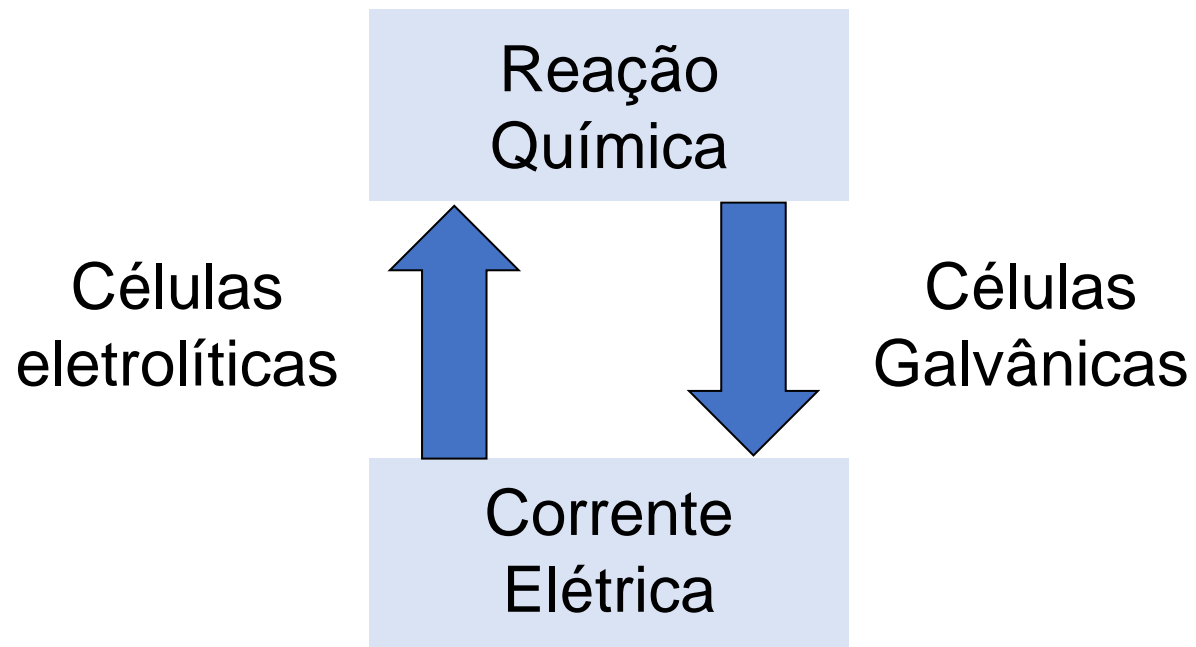
Prof. Dr. Thiago C. Correra

Eletroquímica do equilíbrio

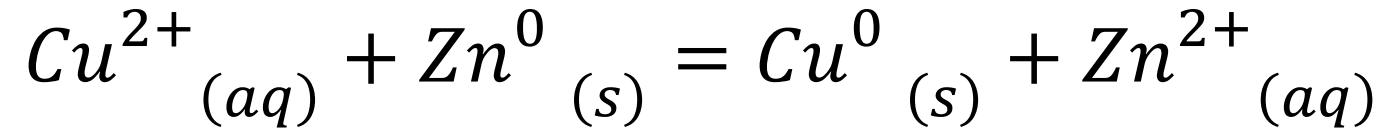
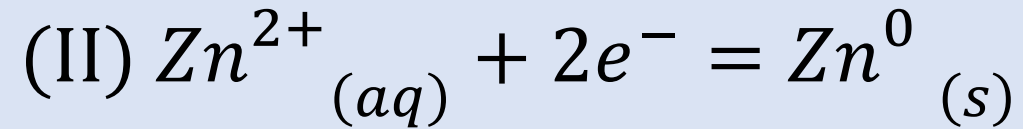
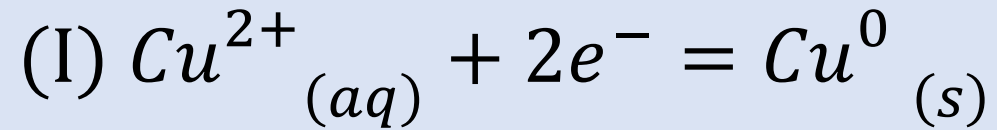
Células eletroquímicas



Trânsferência de elétrons

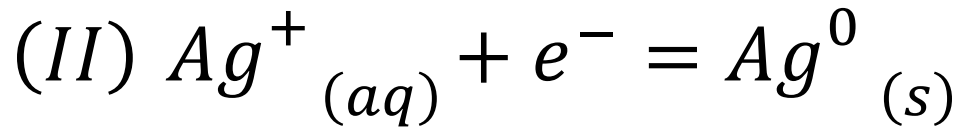
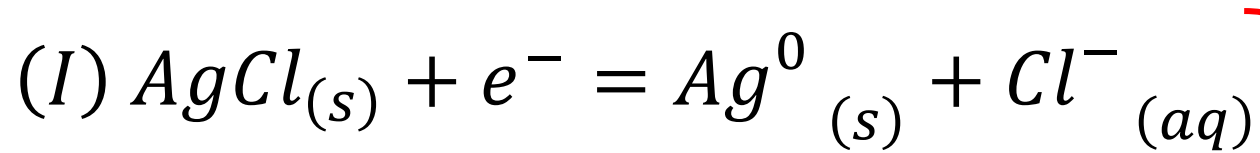
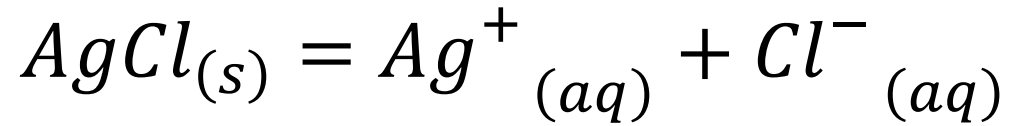


Um exemplo clássico

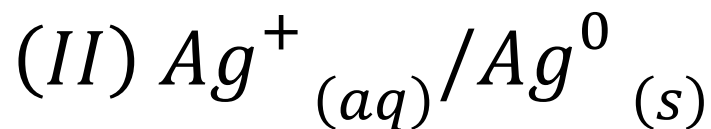
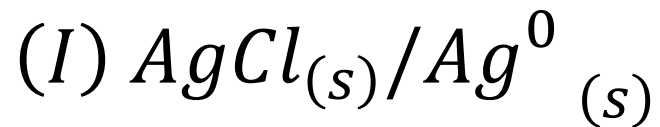


Como obter ΔG , ΔH e ΔS
para essa reação?

Qualquer reação química...

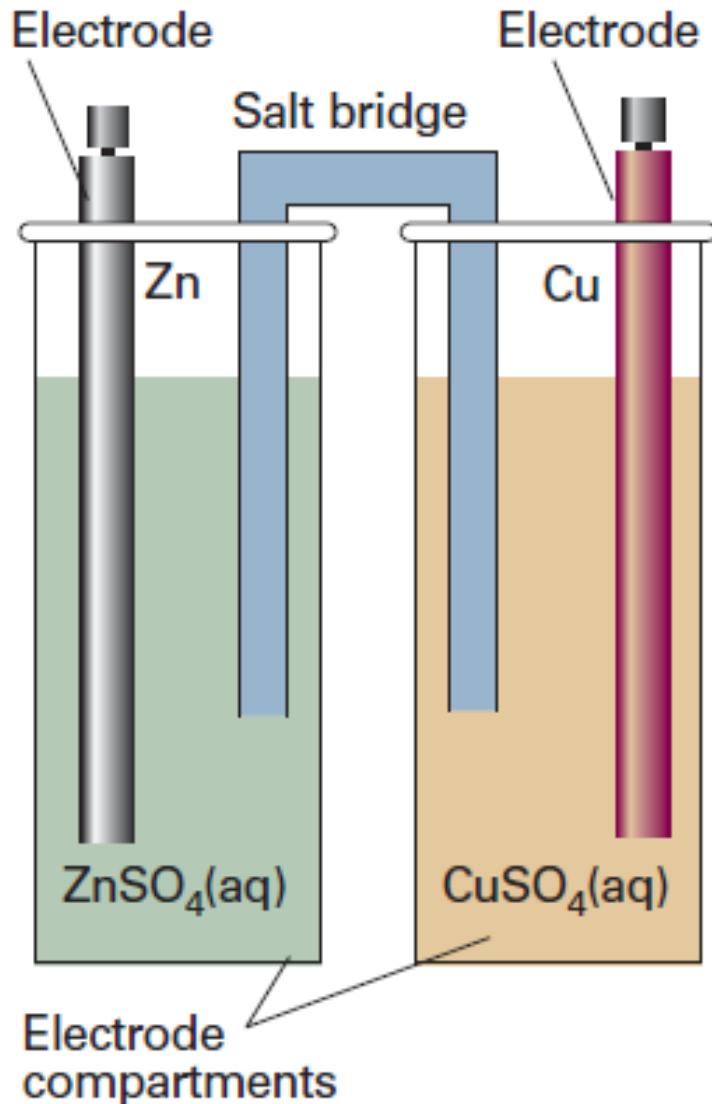
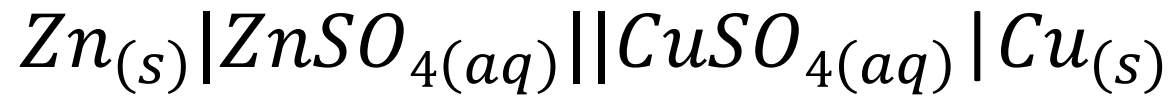


pode ser representada por
semireações de redução

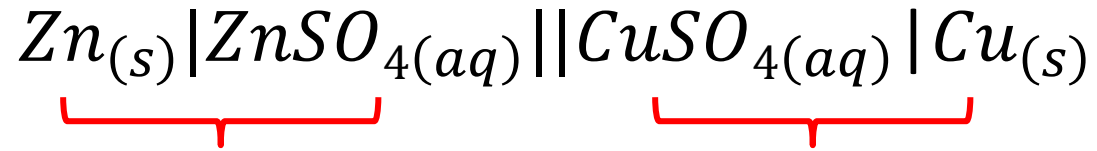


Notação:

oxidado/reduzido

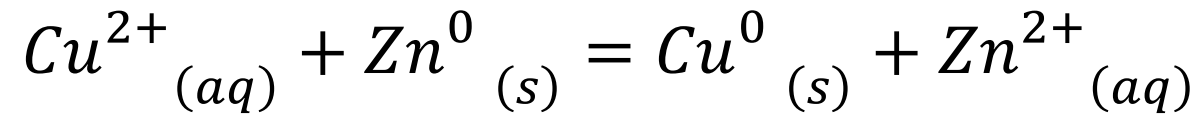
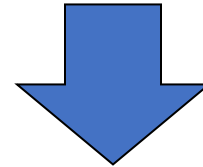


Por convenção:



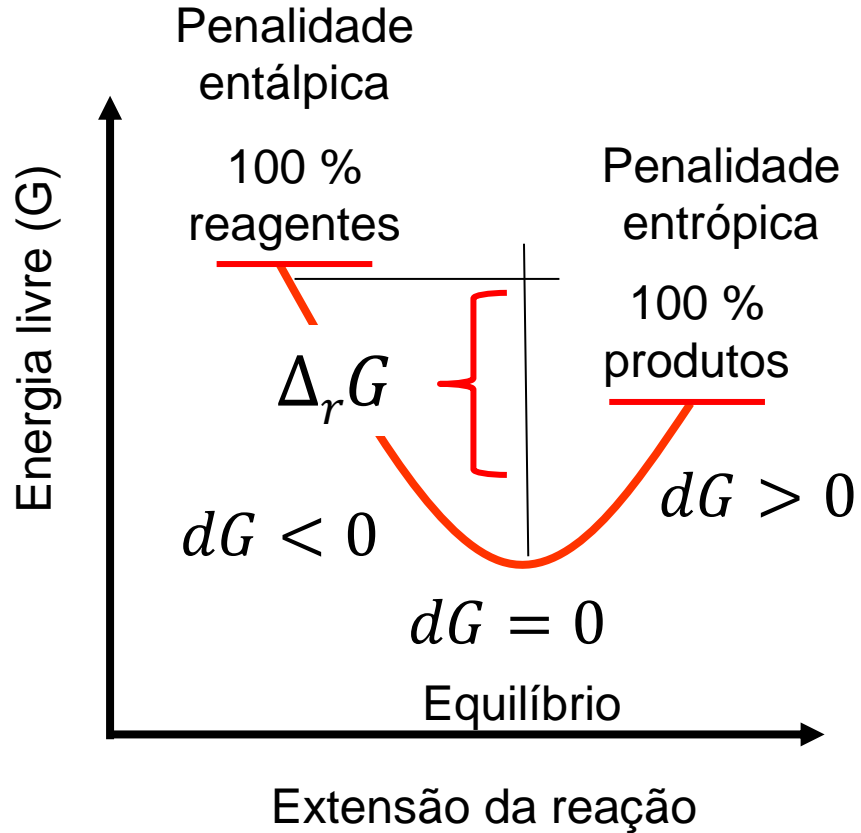
oxidação

redução



Processo espontâneo?

Sistema eletroquímico



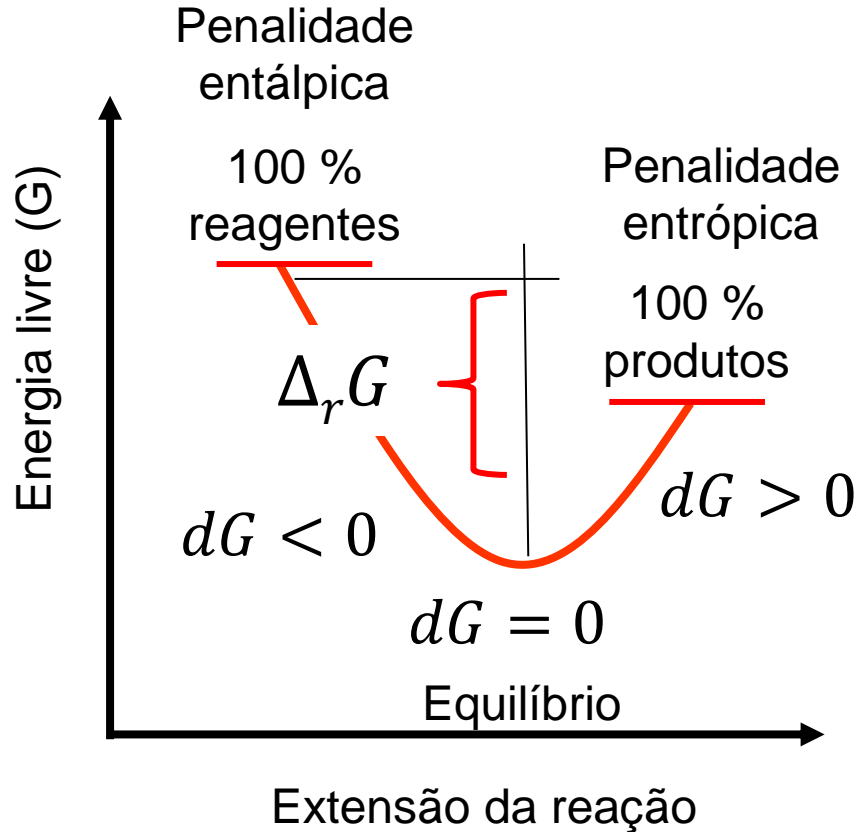
$$dG = \sum_{i=1}^k \bar{G}_i dn_i$$

$$\Delta G = \Delta G^0 + RT \ln Q$$

No equilíbrio: $K = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{eq}$

$$a_i = \gamma_{\pm} \frac{b}{b^0}$$

Termodinâmica de processos eletroquímicos



$$\Delta_r G = w_{elétrico, rev} = w_e$$



$$dG = \sum_{i=1}^k \bar{G}_i dn_i$$

Energia livre liberada poder ser usada para realizar trabalho útil não-PV

Basta obter $\Delta_r G$ reversível e

obtemos o trabalho máximo do processo!

Modelagem termodinâmica


Para um sistema de composição variada que realiza trabalho elétrico além do trabalho mecânico:

$$dG = -SdT + VdP + dw_e + \sum_{i=1}^k \mu_i dn_i$$

Mas para uma célula eletroquímica a T e P constante:

$$dG = dw_e + \sum_{i=1}^k \mu_i dn_i$$

A variação do trabalho elétrico será:

$$dw_e = E_A dq - E_C dq = Edq$$


Carga transportada na presença do potencial E

*deveria ser feita a mesma dedução 2 vezes para potencial anódico e catódico...

Modelagem termodinâmica

No equilíbrio: $dG = dw_e + \sum_{i=1}^k \mu_i dn_i = 0$



$$Edq = -\sum_{i=1}^k \mu_i dn_i = -\frac{d\xi}{\nu_A} \Delta\mu$$

Considerando que o potencial químico será dado por:

$$\mu(T) = \mu_0(T) + RT \ln(a), \quad a = \gamma \frac{b}{b^0}$$

E que a variação de carga dQ é o número de elétrons que reagem durante a reação:

$$dq = -nF \frac{d\xi}{\nu_A}$$

Relação do potencial com equilíbrio

$$Edq = - \sum_{i=1}^k \mu_i dn_i = - \frac{d\xi}{\nu_A} \Delta\mu$$



$$-EnF = \Delta\mu^0 + RT \ln \left(\frac{a_{prod}}{a_{reag}} \right)_{eq}$$

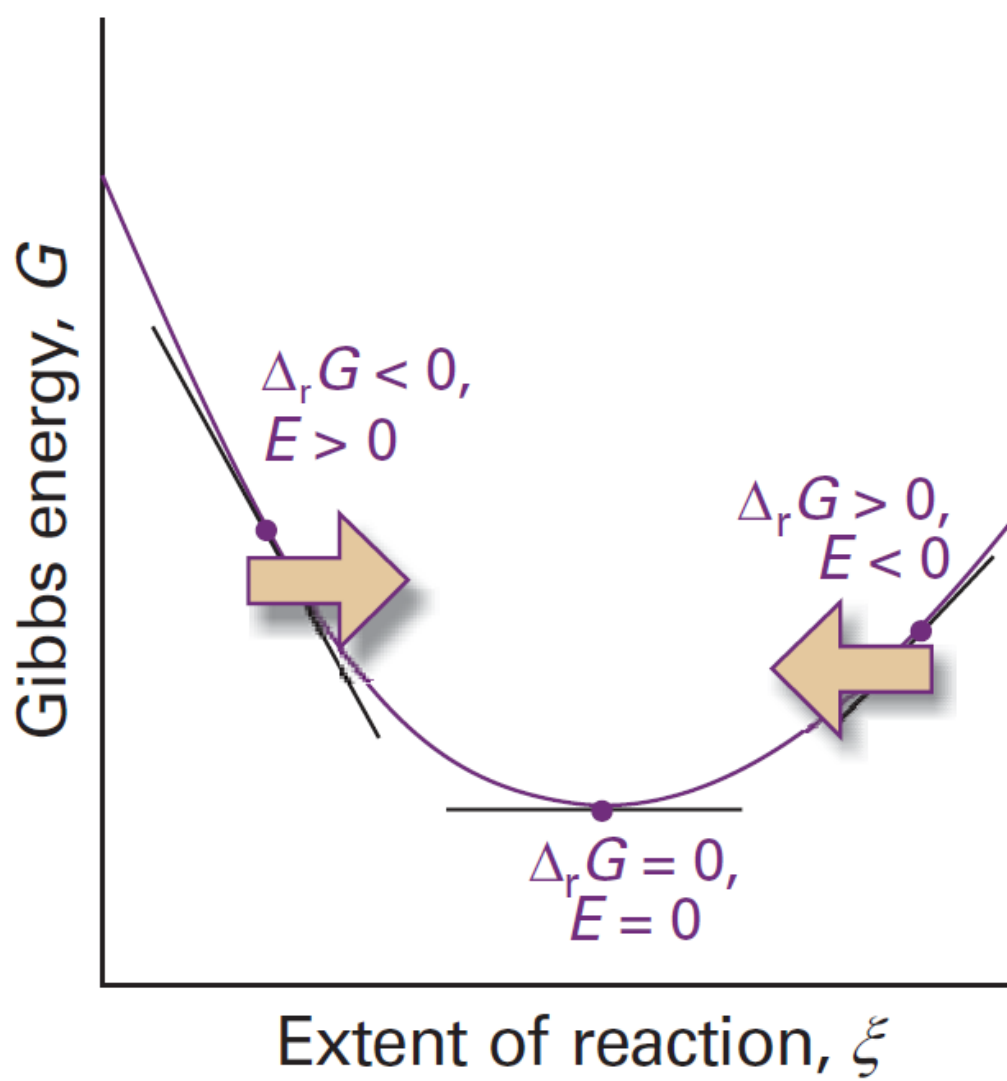


$$E = - \frac{\Delta\mu^0}{nF} - \frac{RT}{nF} \ln K$$

Equação de Nernst:

$$E = E^0 - \frac{RT}{nF} \ln K, \quad E = - \frac{\Delta\mu}{nF}$$

Critérios de equilíbrio

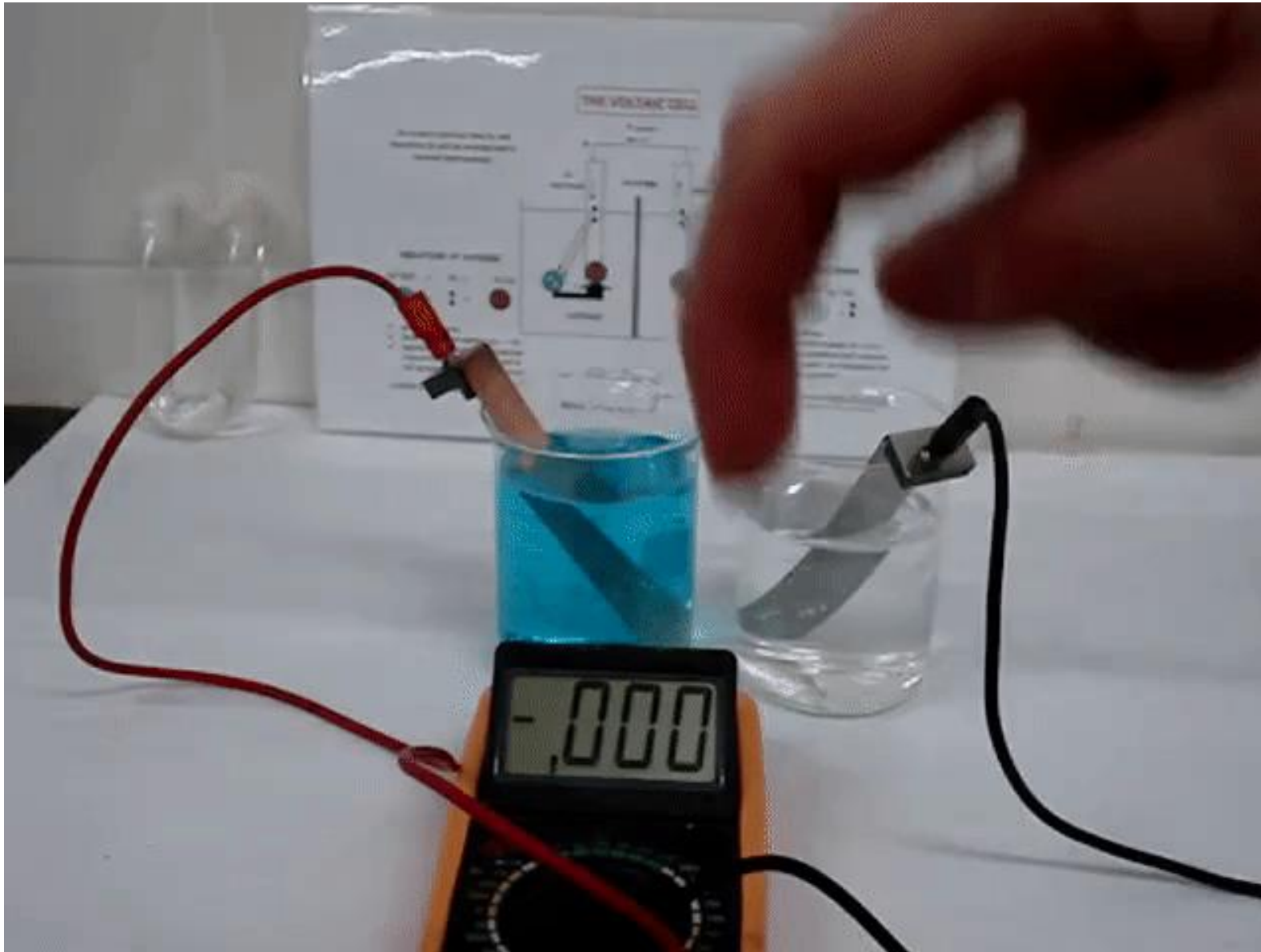


$$E = -\frac{\Delta\mu}{nF} = -\frac{\Delta_r G}{nF}$$



Potencial elétrico é
mais fácil de medir
que potencial químico!

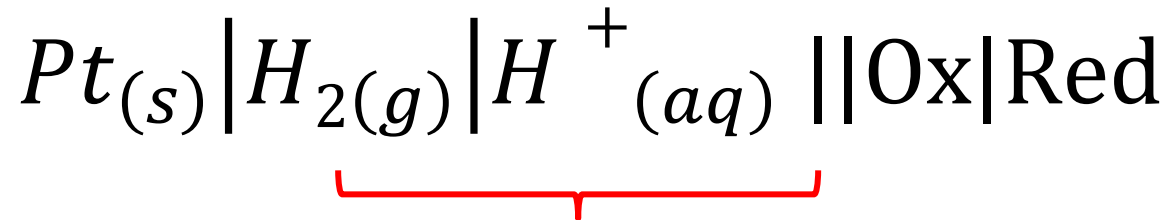
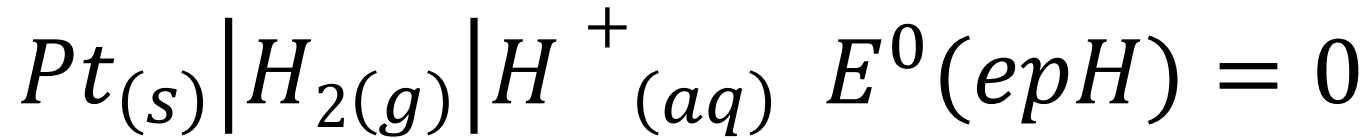
Critérios de equilíbrio



$$E = -\frac{\Delta\mu}{nF} = -\frac{\Delta_r G}{nF}$$

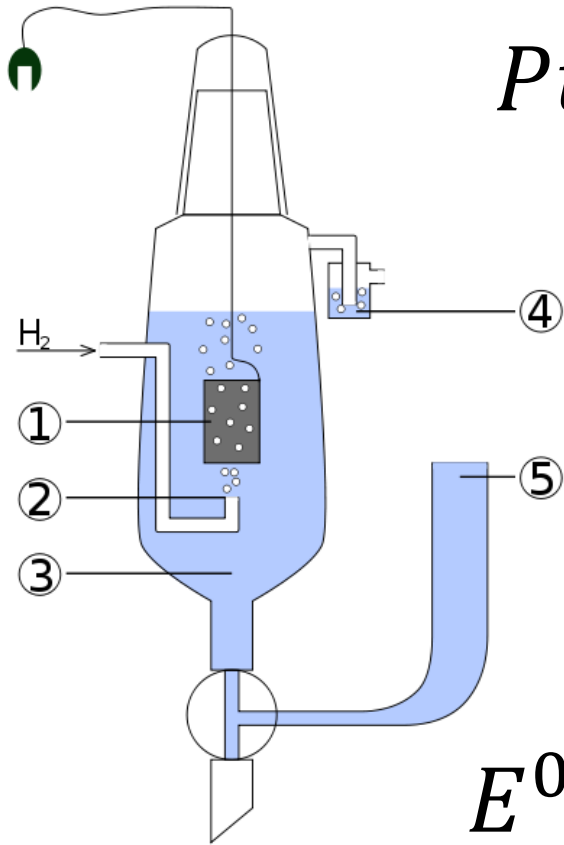
Potencial padrão

Potencial de uma semi-reação pode ser calculado em relação ao potencial padrão (ou absoluto!)



$$E^0 = E^0(Ox|Red) - E^0(epH)$$

$$E^0 = E^0(direita) - E^0(esquerda)$$



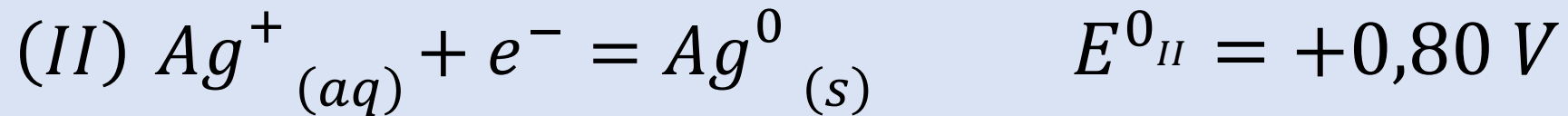
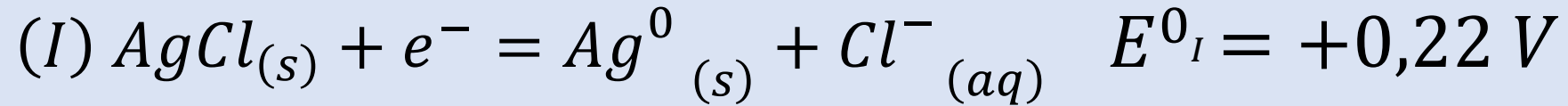
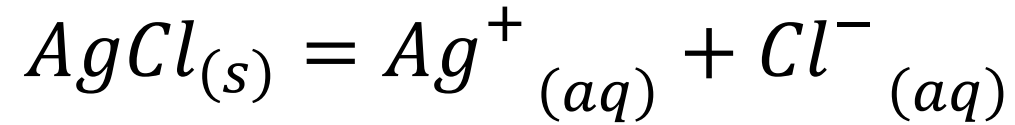
Potenciais padrão

Synoptic Table 7.2* Standard potentials at 298 K

Couple	E^\ominus/V
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2(\text{g})$	0
$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71

* More values are given in the *Data section*.

Equilíbrio de solubilidade

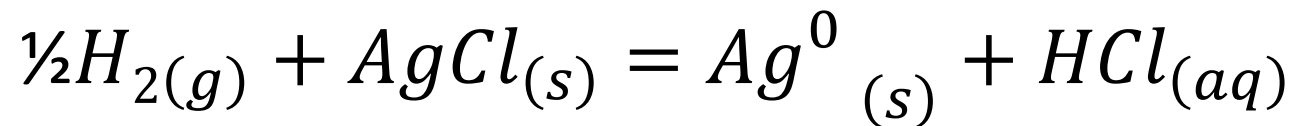
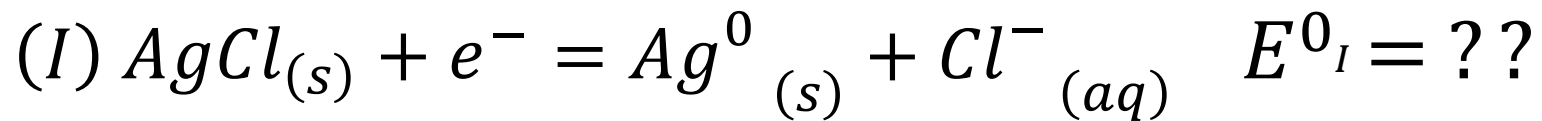


$$E^0 = -0,58 V \quad \ln K = \frac{nFE^0}{RT}, K = 1,6 \cdot 10^{-10}$$

$$K = 1,6 \cdot 10^{-10} = a_{Ag^+} a_{Cl^-} = s^2$$

$$s = 1,3 \cdot 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$$

Obtenção de potenciais padrão



$$E = E^0 - \frac{RT}{F} \ln \left(\frac{a_{H^+} a_{Cl^-}}{(f_{H_2}/P^0)^{1/2}} \right)$$

$$E = E^0 - \frac{RT}{F} \ln(b\gamma_{\pm} b\gamma_{\pm})$$

$$E = E^0 - \frac{RT}{F} \ln(b^2) - \frac{2RT}{F} \ln(\gamma_{\pm})$$

Utilizando Debye-Hückel:

$$\ln \gamma_{\pm} \propto -b^{\frac{1}{2}}, \quad \ln \gamma_{\pm} = -\mathbf{c} b^{\frac{1}{2}},$$

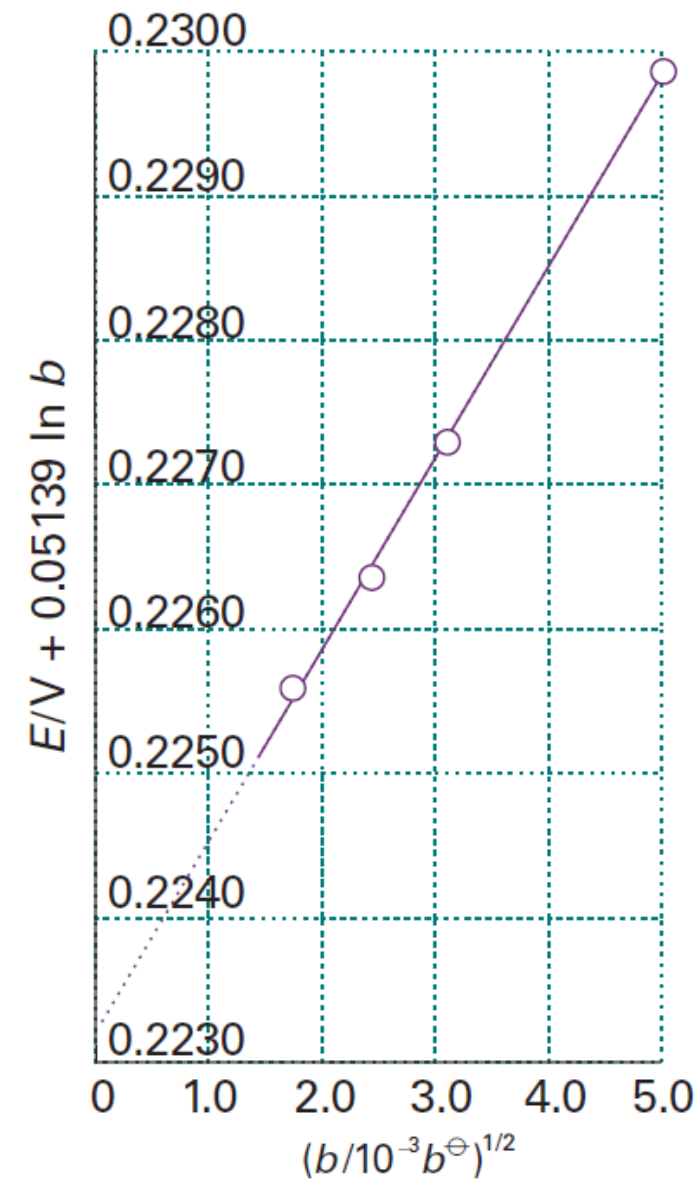
$$E = E^0 - \frac{RT}{F} \ln(b^2) - \frac{2RT}{F} \ln(\gamma_{\pm})$$

$$E + \frac{RT}{F} \ln(b^2) = E^0 + \underbrace{\frac{2RT}{F} \mathbf{c} b^{\frac{1}{2}}}$$

$$E + \frac{RT}{F} \ln(b^2) = E^0 + \mathbf{C} b^{\frac{1}{2}}$$

Podemos determinar E para
diversas molalidades

Obtenção de potenciais padrão



$$E + \frac{2RT}{F} \ln(b) = E^0 + C b^{\frac{1}{2}}$$

$$\lim_{b \rightarrow 0} E^0 = E + \frac{2RT}{F} \ln(b) - \cancel{C b^{\frac{1}{2}}}$$

$$E - E^0 + \frac{2RT}{F} \ln b = \frac{2RT}{F} \ln(\gamma_{\pm})$$

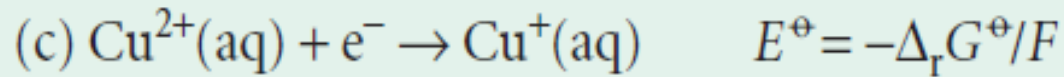
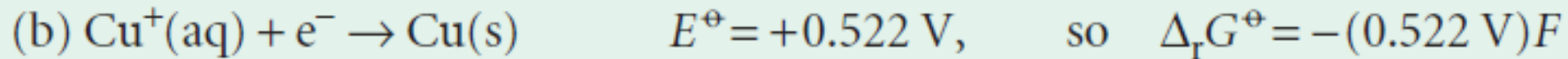
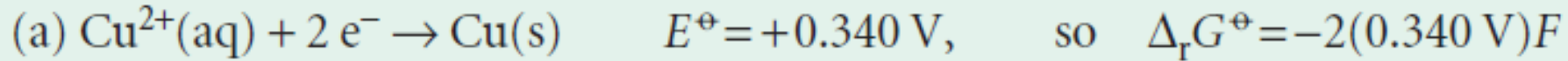
$$\frac{E - E^0}{2RT/F} - \ln b = \ln(\gamma_{\pm})$$

Obtenção de E^0 e do
coeficiente de atividade

Pequeno aviso sobre E

Example 7.4 *Evaluating a standard potential from two others*

Given that the standard potentials of the Cu^{2+}/Cu and Cu^+/Cu couples are +0.340 V and +0.522 V, respectively, evaluate $E^\ominus(\text{Cu}^{2+}, \text{Cu}^+)$.



Because (c) = (a) – (b), the standard Gibbs energy of reaction (c) is

$$\Delta_r G^\ominus = \Delta_r G^\ominus(\text{a}) - \Delta_r G^\ominus(\text{b}) = -(-0.158 \text{ V}) \times F$$

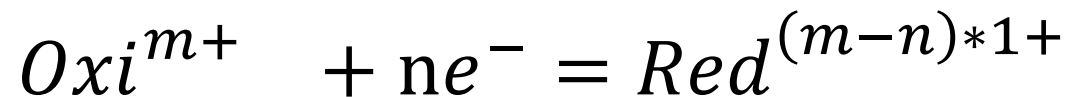
Therefore, $E^\ominus = +0.158 \text{ V}$. Note that the generalization of the calculation we just performed is

$$v_c E^\ominus(\text{c}) = v_a E^\ominus(\text{a}) + v_b E^\ominus(\text{b}) \quad (7.34)$$

Genericamente

$$E = E^0 - \frac{RT}{nF} \ln(b) - \frac{RT}{nF} \ln(\gamma_{\pm})$$

Medindo contra o eletrodo padrão de hidrogênio:



$$\Delta G^0(T) = -nFE^0(T)$$

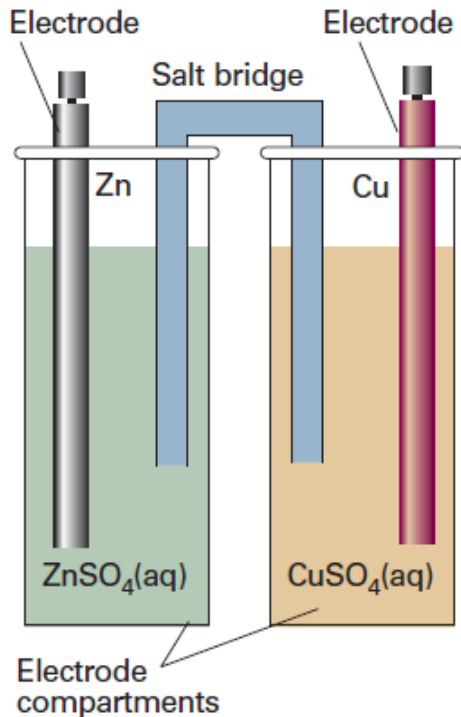
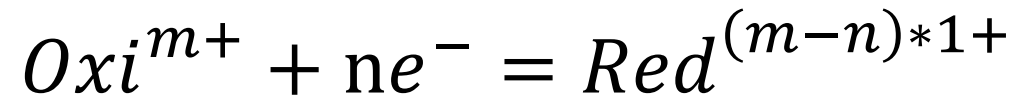
$$\left(\frac{\partial \Delta G^0(T)}{\partial T} \right)_{P,ni} = -\Delta S^0(T) = nF \left(\frac{\partial E^0(T)}{\partial T} \right)_{P,ni}$$

$$\Delta H^0(T) = \Delta G^0(T) + T\Delta S^0(T)$$

Genericamente

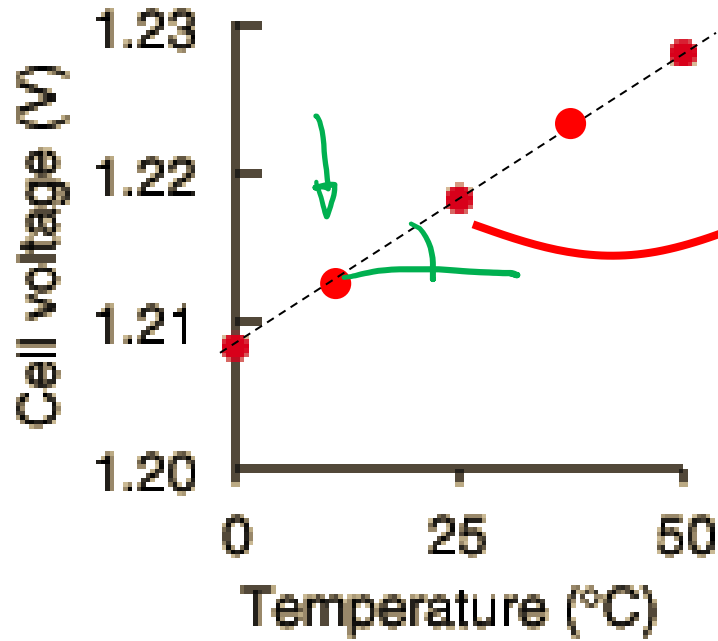
$$E = E^0 - \frac{RT}{nF} \ln(b) - \frac{RT}{nF} \ln(\gamma_{\pm})$$

Medindo contra o eletrodo padrão de hidrogênio:

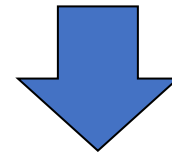


E^0 / V	T / K	K
-0,32	298,15	$4,1 \cdot 10^{-6}$
-0,28	308,15	:
-0,16	:	
:		

Dependencia de E com temperatura



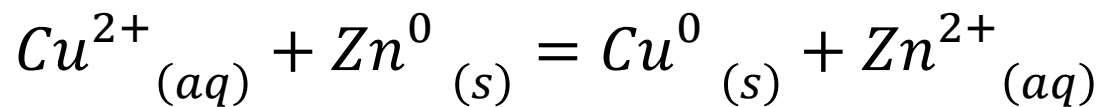
$$\Delta S(T) = -nF \frac{dE(T)}{dT}$$



Para um curto intervalo de temperatura ΔS pode ser considerado constante

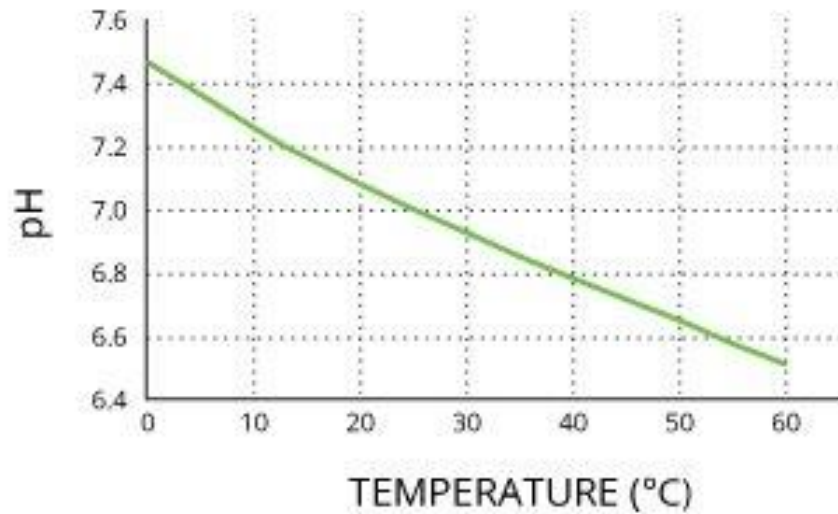
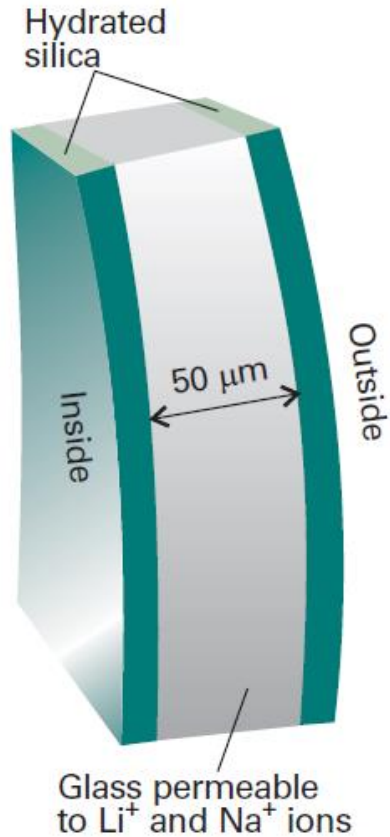
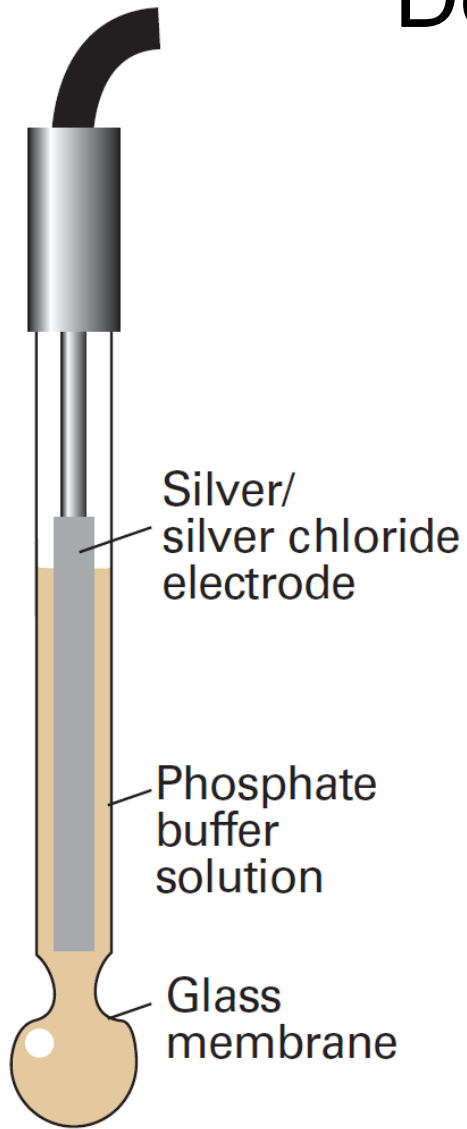
For ion concentrations

Zn^{2+} 10^{-5} M, Cu^{2+} 0.1 M



Determinação de constantes de equilíbrio

$$\ln K(T) = \frac{\Delta G^0(T)}{RT} = - \frac{nFE^0(T)}{RT}$$



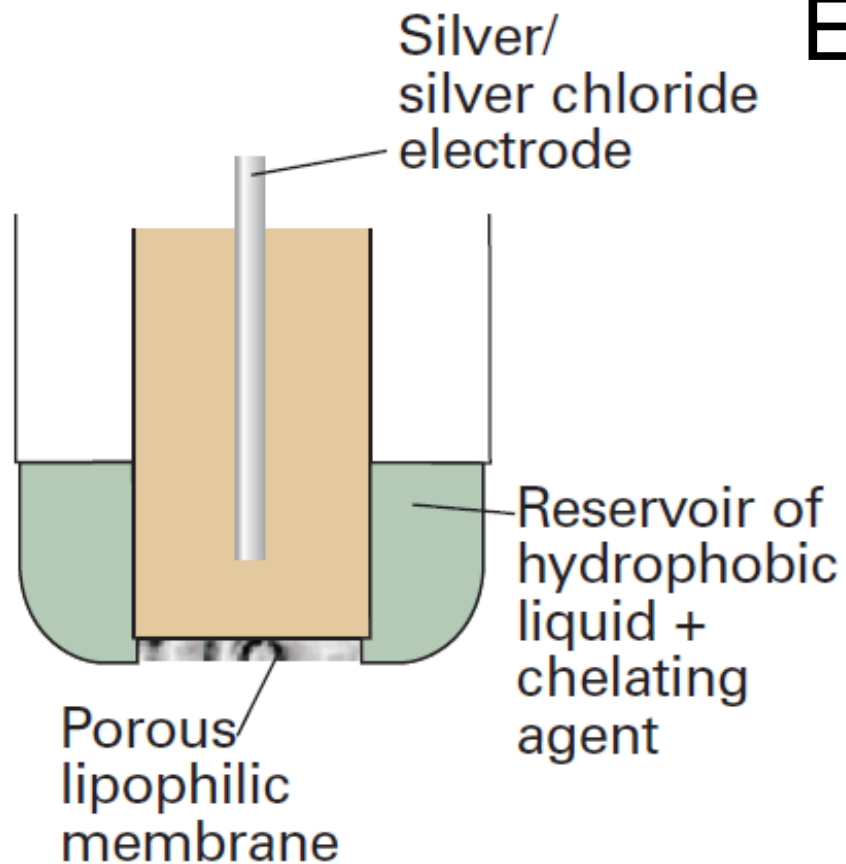
<https://www.splabor.com.br>

Eletrodos seletivos

Membrana pode ser funcionalizada para ter sensibilidade a uma determinada espécie



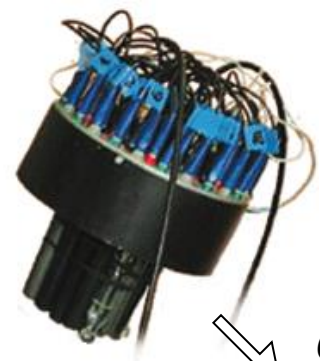
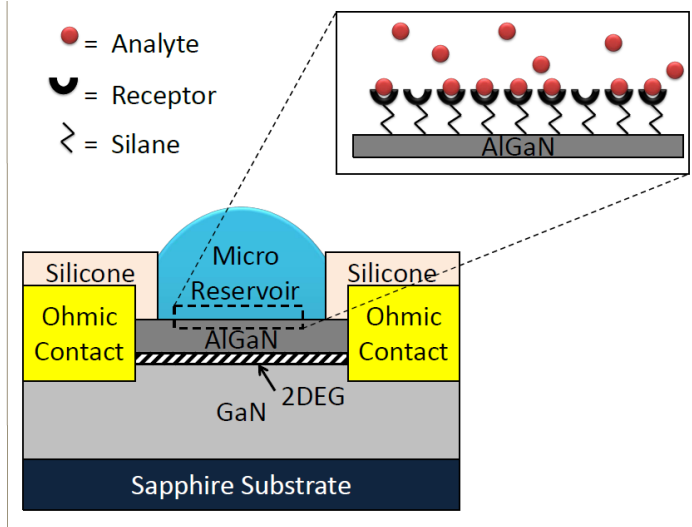
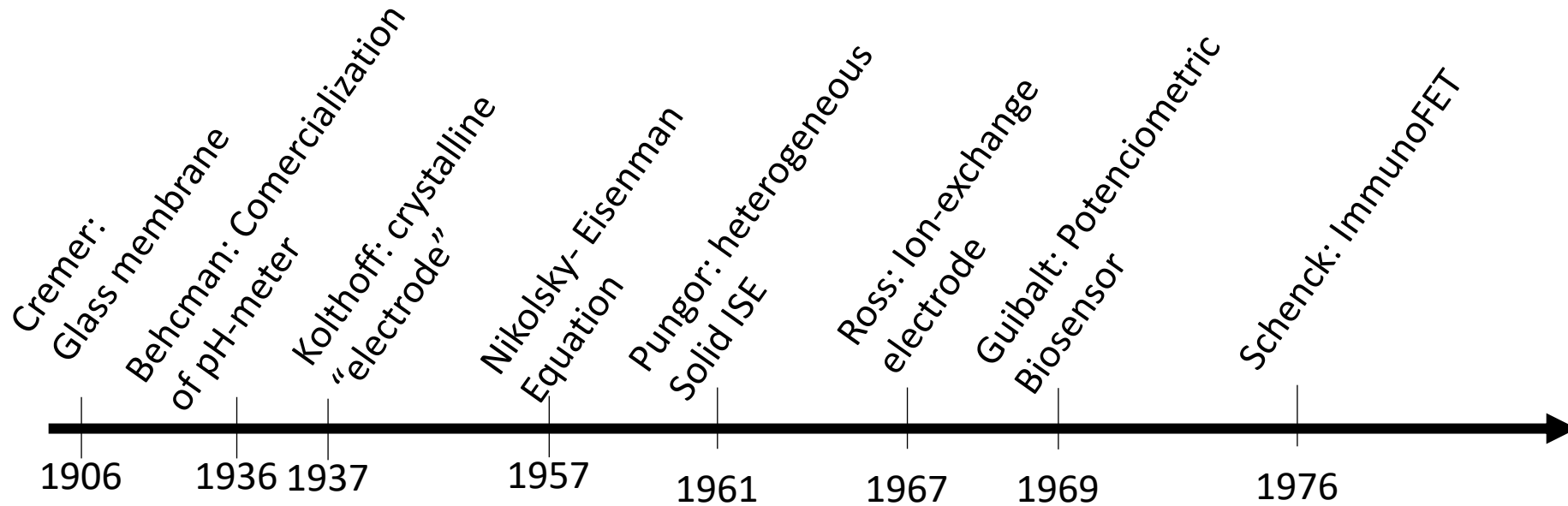
Seletividade



Equação de Nikolsky-Eisenman

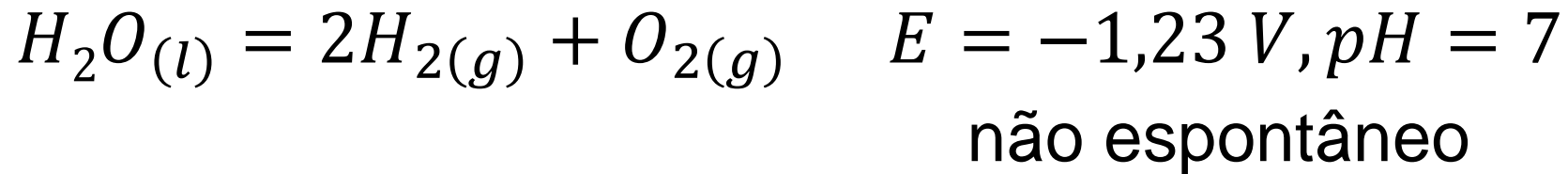
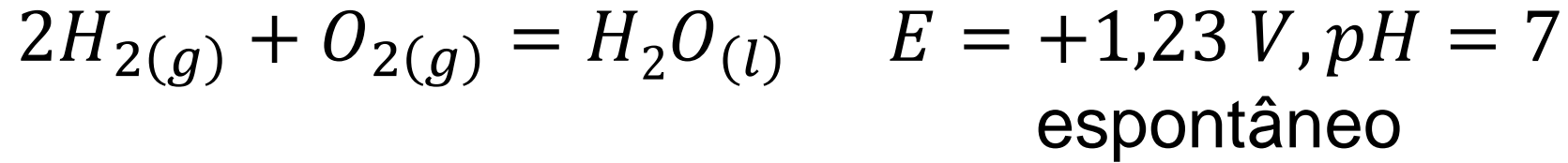
$$E = E^0 + \frac{RT}{z_i F} \ln \left[a_i + \sum_j K_{ij} (a_j)^{z_i/z_j} \right]$$

Linguas eletrônicas



Coffea Arabica
Coffea Canephora

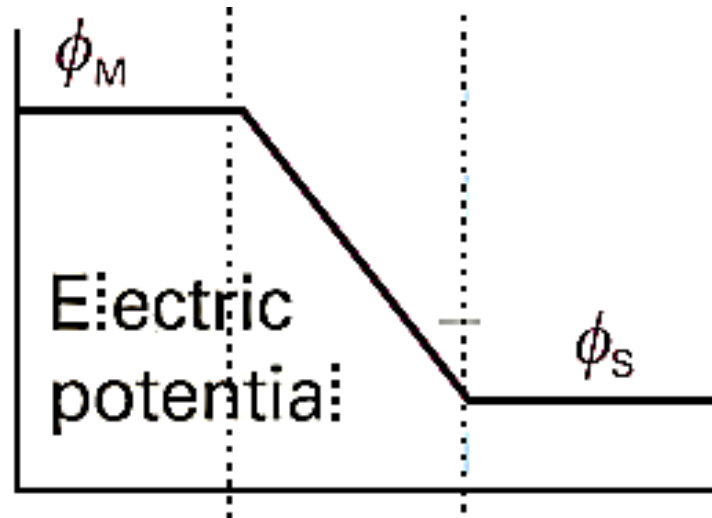
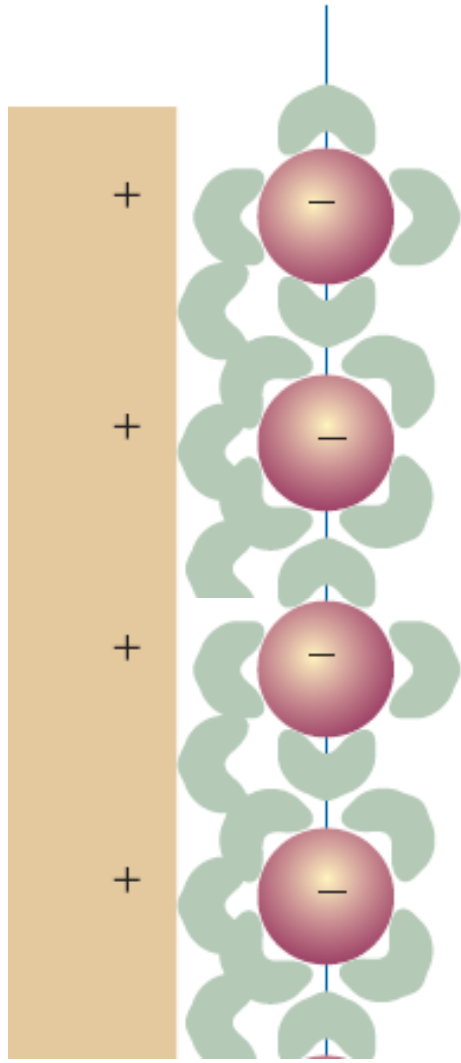
Células eletrolíticas



Para ocorrer a eletrólise da água precisamos aplicar cerca de **1,8 V**, e não 1,23 V!

Sobrepotencial oriundo
da polarização,
transporte de íons, etc...

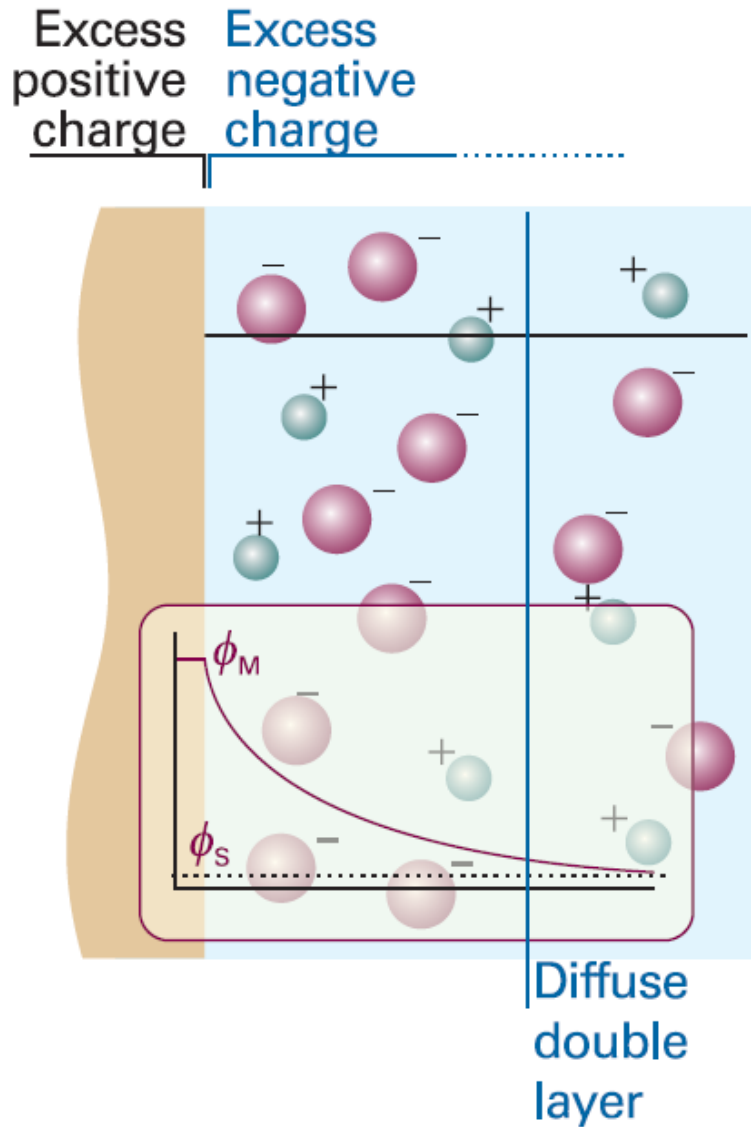
Interface eletrodo-solução



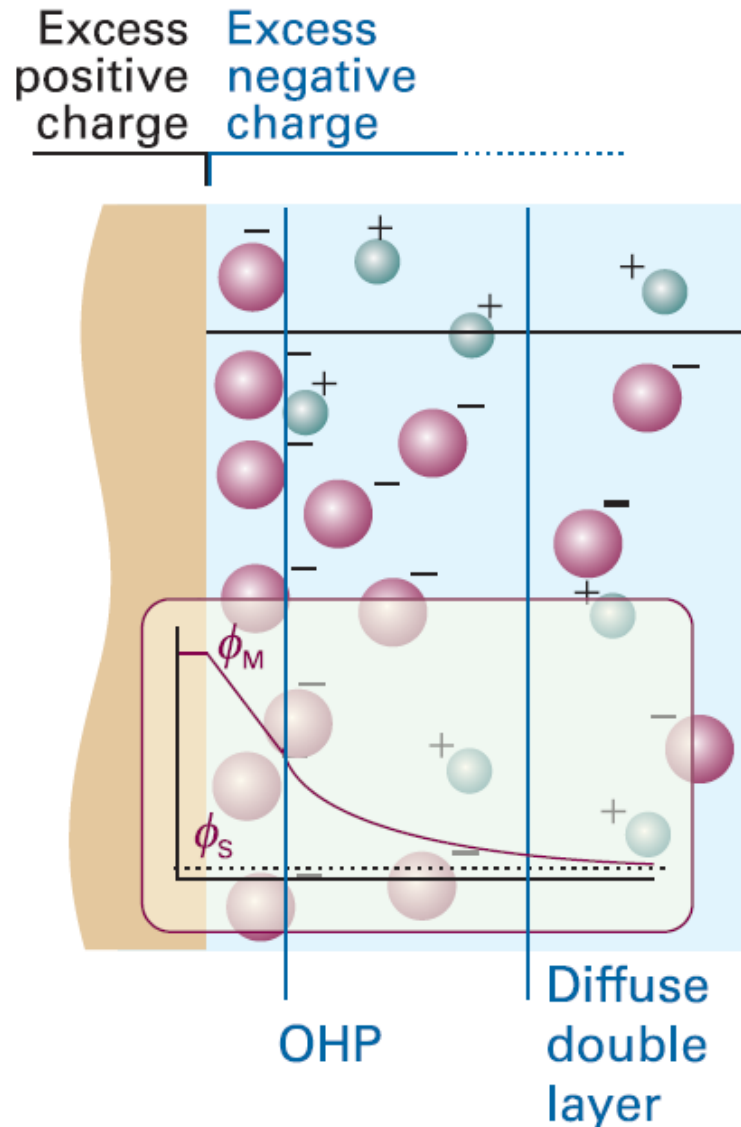
Modelo da camada de Helmholtz
– camada fixa de contra-íons

Outros modelos ...

Interface eletrodo-solução



Gouy-Chapman



Stern

Sobrepotencial

Sobrepotencial é gerado por efeitos que requerem trabalho para que ocorram:

- Ativação
- Queda ôhmica
- Polarização por concentração

Energia que deve ser fornecida para eletrólise, na forma de energia livre, deverá compensar a não-espontaneidade do processo e o sobrepotencial associado ao sistema!