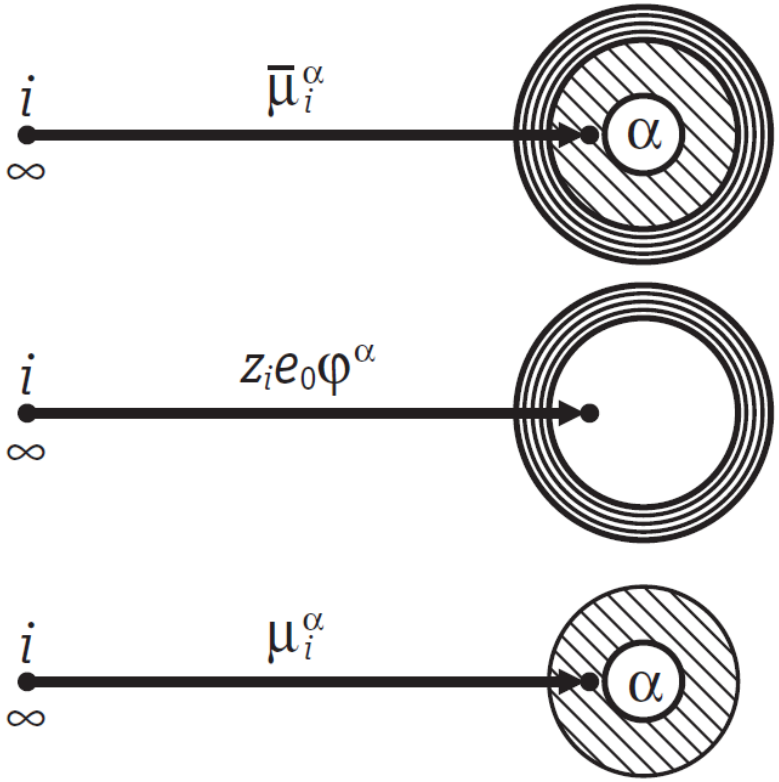
Электрохимическая термодинамика

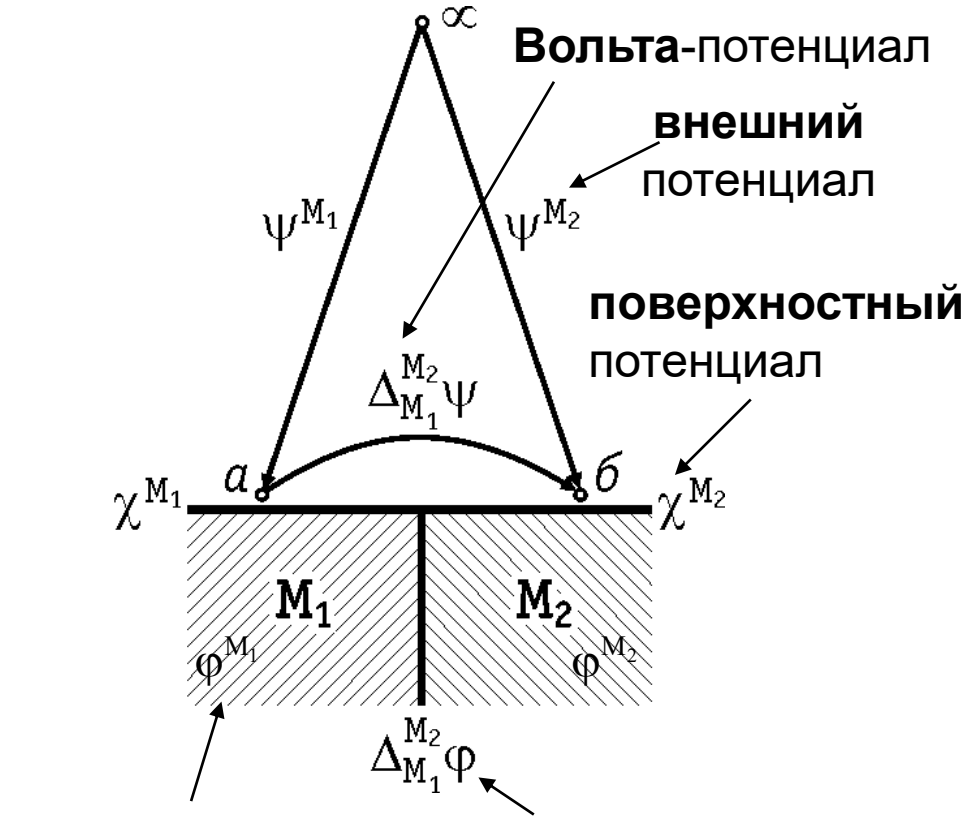
Равновесие на границе электрод/раствор

$$d\bar{G} = -SdT + VdP + \sum_i \mu_i dN_i + F\sum_i z_i \varphi dN_i$$

$$\bar{\mu}_i = \left(\frac{\partial \bar{G}}{\partial N_i}\right)_{p,T,N_{j\neq i}} = \mu_i + z_i F \varphi$$



$$\varphi^\alpha = \psi^\alpha + \chi^\alpha$$



Равновесие на границе электрод/раствор

$$\bar{\mu}_i^{\beta} - \bar{\mu}_i^{\alpha} = (\mu_i^{\beta} - \mu_i^{\alpha}) + z_i F(\varphi^{\beta} - \varphi^{\alpha})$$

- Электрическую разность потенциалов можно измерить только между точками в одной фазе

- **Граница двух металлов:**

$$e^-(M_1) \rightleftharpoons e^-(M_2) \rightarrow \bar{\mu}_e^{M_1} = \bar{\mu}_e^{M_2} \rightarrow \mu_e^{M_1} - F\varphi^{M_1} = \mu_e^{M_2} - F\varphi^{M_2} \rightarrow$$

$$\rightarrow \Delta_{M_1}^{M_2}\varphi = \varphi^{M_2} - \varphi^{M_1} = \frac{\mu_e^{M_2} - \mu_e^{M_1}}{F}$$

- **Граница металл/раствор:** $M^{z+}(\text{металл}) \rightleftharpoons M^{z+}(\text{раствор})$

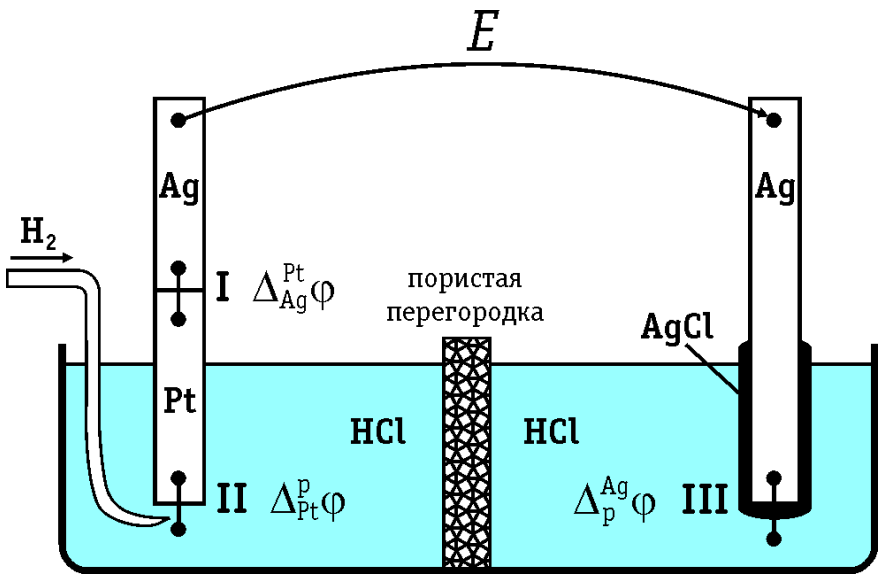
$$\bar{\mu}_{M^{z+}}^{M} = \bar{\mu}_{M^{z+}}^{p} \rightarrow \mu_{M^{z+}}^{M} + z_+F\varphi^M = \mu_{M^{z+}}^{p} + z_+F\varphi^p \rightarrow$$

$$\rightarrow \Delta_p^M\varphi = \varphi^M - \varphi^p = \frac{\mu_{M^{z+}}^{p} - \mu_{M^{z+}}^{M}}{z_+F} \rightarrow \mu_{M^{z+}}^{p} = \mu_{M^{z+}}^{0,p} + RT\ln a_{M^{z+}}$$

$$\boxed{\Delta_p^M\varphi = \text{const} + \frac{RT}{z_+F}\ln a_{M^{z+}}}$$

(Уравнение Нернста, 1889 г.)

ЭДС электрохимической цепи



Равновесная э/х цепь: электрохимическое равновесие наблюдается на каждой фазовой границе, а разность потенциалов на концах цепи *E* скомпенсирована разностью потенциалов от внешнего источника тока

Электродвижущая сила (E) – разность потенциалов на концах равновесной электрохимической цепи

$$E = E_{\text{пр}} - E_{\text{л}}$$

$e^-(Ag) \leftrightarrow e^-(Pt)$ $\quad \Delta_{Ag}^{Pt}\varphi = \dfrac{\mu_e^{Pt} - \mu_e^{Ag}}{F}$

$1/2H_2 \leftrightarrow H_{адс} \leftrightarrow e^-(Pt) + H^+$ $\quad \Delta_{Pt}^{p}\varphi = \dfrac{1}{F}\left(\dfrac{1}{2}\mu_{H_2} - \mu_e^{Pt} - \mu_{H^+}^{p}\right)$

$AgCl + e^-(Ag) \leftrightarrow Ag + Cl^-$ $\quad \Delta_{p}^{Ag}\varphi = \dfrac{1}{F}(\mu_{AgCl} + \mu_e^{Ag} - \mu_{Cl^-}^{p} - \mu_{Ag})$

$AgCl + 1/2H_2 \leftrightarrow Ag + HCl$ $\quad E = \dfrac{1}{F}\left(\dfrac{1}{2}\mu_{H_2} + \mu_{AgCl} - \mu_{HCl} - \mu_{Ag}\right) = \dfrac{-\Delta G}{F}$

- Уравнение Нернста для ЭДС электрохимической цепи:

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{\prod a_i^{\nu_i}}{\prod a_j^{\nu_j}}\right)$$

- Температурный коэффициент ЭДС:

$$\frac{dE}{dt} = \frac{\Delta S}{nF}$$

Таблицы электродных потенциалов

Handbook of Chemistry and Physics / Electrochemical series

Reaction	E°/V
$Ac^{3+} + 3\,e \rightleftharpoons Ac$	−2.20
$Ag^+ + e \rightleftharpoons Ag$	0.7996
$Ag^{2+} + e \rightleftharpoons Ag^+$	1.980
$Ag(ac) + e \rightleftharpoons Ag + (ac)^-$	0.643
$AgBr + e \rightleftharpoons Ag + Br^-$	0.07133
$AgBrO_3 + e \rightleftharpoons Ag + BrO_3^-$	0.546
$Ag_2C_2O_4 + 2\,e \rightleftharpoons 2\,Ag + C_2O_4^{2-}$	0.4647
$AgCl + e \rightleftharpoons Ag + Cl^-$	0.22233
$AgCN + e \rightleftharpoons Ag + CN^-$	−0.017
$Ag_2CO_3 + 2\,e \rightleftharpoons 2\,Ag + CO_3^{2-}$	0.47
$Ag_2CrO_4 + 2\,e \rightleftharpoons 2\,Ag + CrO_4^{2-}$	0.4470
$AgF + e \rightleftharpoons Ag + F^-$	0.779
$Ag_4[Fe(CN)_6] + 4\,e \rightleftharpoons 4\,Ag + [Fe(CN)_6]^{4-}$	0.1478
$AgI + e \rightleftharpoons Ag + I^-$	−0.15224
$AgIO_3 + e \rightleftharpoons Ag + IO_3^-$	0.354
$Ag_2MoO_4 + 2\,e \rightleftharpoons 2\,Ag + MoO_4^{2-}$	0.4573
$AgNO_2 + e \rightleftharpoons Ag + 2\,NO_2^-$	0.564
$Ag_2O + H_2O + 2\,e \rightleftharpoons 2\,Ag + 2\,OH^-$	0.342
$Ag_2O_3 + H_2O + 2\,e \rightleftharpoons 2\,AgO + 2\,OH^-$	0.739
$Ag^{3+} + 2\,e \rightleftharpoons Ag^+$	1.9
$Ag^{3+} + e \rightleftharpoons Ag^{2+}$	1.8
$Ag_2O_2 + 4\,H^+ + e \rightleftharpoons 2\,Ag + 2\,H_2O$	1.802
$2\,AgO + H_2O + 2\,e \rightleftharpoons Ag_2O + 2\,OH^-$	0.607
$AgOCN + e \rightleftharpoons Ag + OCN^-$	0.41
$Ag_2S + 2\,e \rightleftharpoons 2\,Ag + S^{2-}$	−0.691
$Ag_2S + 2\,H^+ + 2\,e \rightleftharpoons 2\,Ag + H_2S$	−0.0366
$AgSCN + e \rightleftharpoons Ag + SCN^-$	0.08951
$Ag_2SeO_3 + 2\,e \rightleftharpoons 2\,Ag + SeO_4^{2-}$	0.3629

Reaction	E°/V
$Al(OH)_4^- + 3\,e \rightleftharpoons Al + 4\,OH^-$	−2.328
$H_2AlO_3^- + H_2O + 3\,e \rightleftharpoons Al + 4\,OH^-$	−2.33
$AlF_6^{3-} + 3\,e \rightleftharpoons Al + 6\,F^-$	−2.069
$Am^{4+} + e \rightleftharpoons Am^{3+}$	2.60
$Am^{2+} + 2\,e \rightleftharpoons Am$	−1.9
$Am^{3+} + 3\,e \rightleftharpoons Am$	−2.048
$Am^{3+} + e \rightleftharpoons Am^{2+}$	−2.3
$As + 3\,H^+ + 3\,e \rightleftharpoons AsH_3$	−0.608
$As_2O_3 + 6\,H^+ + 6\,e \rightleftharpoons 2\,As + 3\,H_2O$	0.234
$HAsO_2 + 3\,H^+ + 3\,e \rightleftharpoons As + 2\,H_2O$	0.248
$AsO_2^- + 2\,H_2O + 3\,e \rightleftharpoons As + 4\,OH^-$	−0.68
$H_3AsO_4 + 2\,H^+ + 2\,e^- \rightleftharpoons HAsO_2 + 2\,H_2O$	0.560
$AsO_4^{3-} + 2\,H_2O + 2\,e \rightleftharpoons AsO_2^- + 4\,OH^-$	−0.71
$At_2 + 2\,e \rightleftharpoons 2\,At^-$	0.3
$Au^+ + e \rightleftharpoons Au$	1.692
$Au^{3+} + 2\,e \rightleftharpoons Au^+$	1.401
$Au^{3+} + 3\,e \rightleftharpoons Au$	1.498
$Au^{2+} + e^- \rightleftharpoons Au^+$	1.8
$AuOH^{2+} + H^+ + 2\,e \rightleftharpoons Au^+ + H_2O$	1.32
$AuBr_2^- + e \rightleftharpoons Au + 2\,Br^-$	0.959
$AuBr_4^- + 3\,e \rightleftharpoons Au + 4\,Br^-$	0.854
$AuCl_4^- + 3\,e \rightleftharpoons Au + 4\,Cl^-$	1.002
$Au(OH)_3 + 3\,H^+ + 3\,e \rightleftharpoons Au + 3\,H_2O$	1.45
$H_2BO_3^- + 5\,H_2O + 8\,e \rightleftharpoons BH_4^- + 8\,OH^-$	−1.24
$H_2BO_3^- + H_2O + 3\,e \rightleftharpoons B + 4\,OH^-$	−1.79
$H_3BO_3 + 3\,H^+ + 3\,e \rightleftharpoons B + 3\,H_2O$	−0.8698
$B(OH)_3 + 7\,H^+ + 8\,e \rightleftharpoons BH_4^- + 3\,H_2O$	−0.481
$Ba^{2+} + 2\,e \rightleftharpoons Ba$	−2.912

Электродный потенциал

Pt, H_2 , p = 1 атм | HA, $a_\pm$=1 ⁝ MA | M | Pt

$$\mathrm{Ox_1} + \mathrm{Red_2} = \mathrm{Red_1} + \mathrm{Ox_2} \qquad E_3$$

$$1:\ \mathrm{Ox_1} + e^- = \mathrm{Red_1}$$

$$2:\ \mathrm{Ox_2} + e^- = \mathrm{Red_2}$$

Pt, H_2 | HCl ⁝ раствор (I) | M_1 | Pt

Pt, H_2 | HCl ⁝ раствор (I) | M_2 | Pt

$$E_1: \qquad \mathrm{Ox_1} + \frac{1}{2}\,\mathrm{H_2} = \mathrm{Red_1} + \mathrm{H^+}$$

$$E_2: \qquad \mathrm{Ox_2} + \frac{1}{2}\,\mathrm{H_2} = \mathrm{Red_2} + \mathrm{H^+}$$

Стандартные электродные потенциалы
(p = 1 атм, t = 25 °C, a = 1 моль/л)