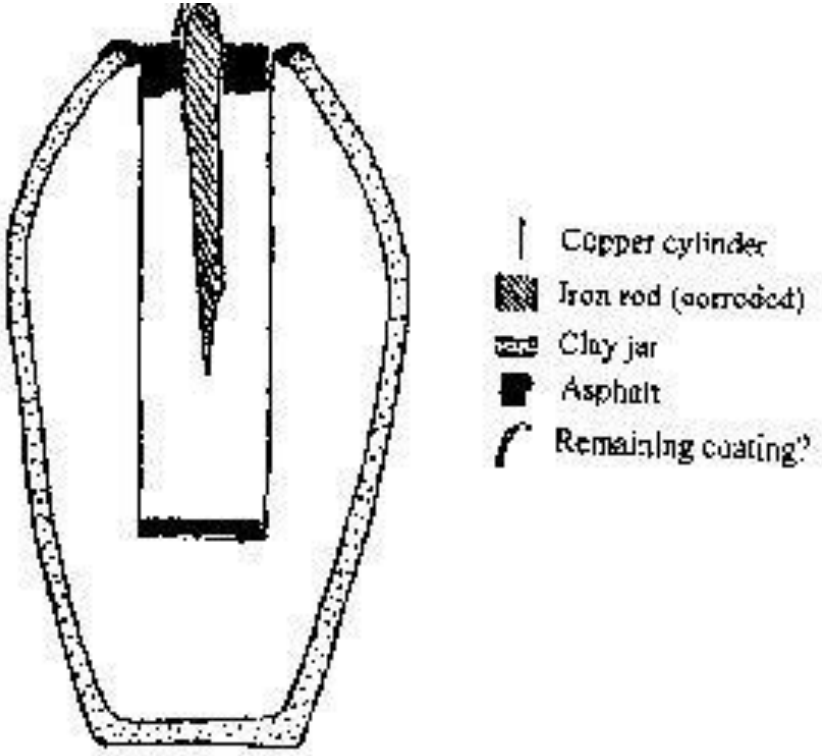
Гальванические элементы

Луиджи Гальвани 1791г.

Алессандро Вольта 1800г.

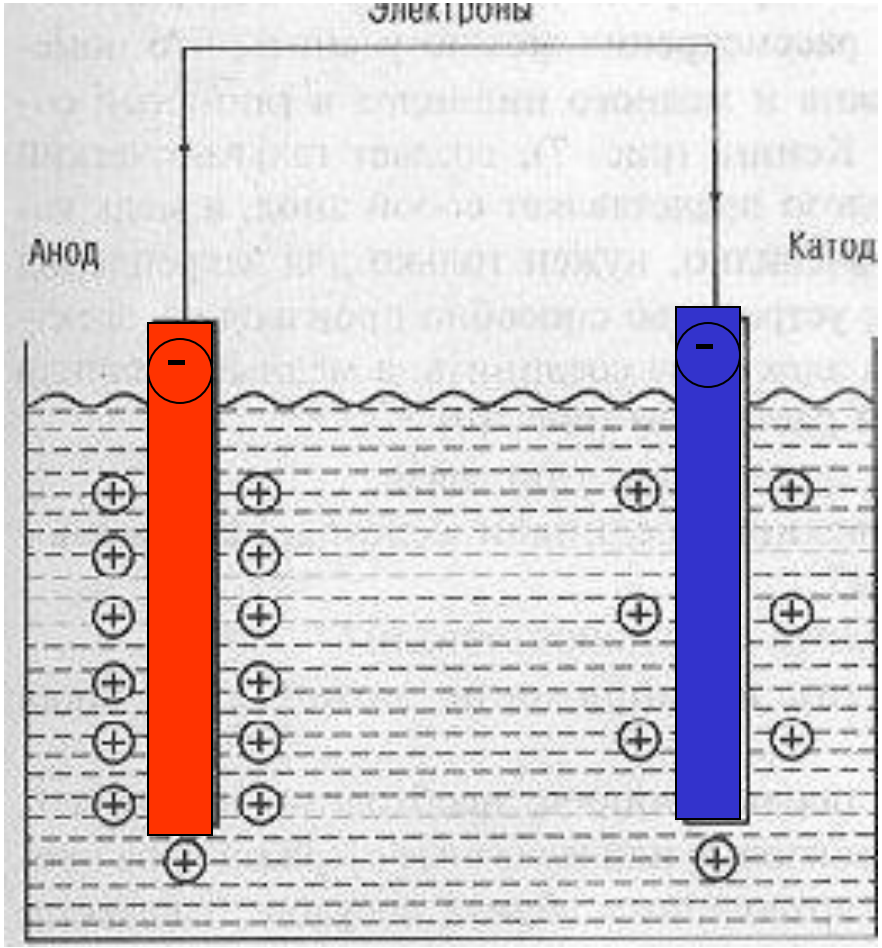
Парфянская батарея

Электрический ток 2000 лет назад???

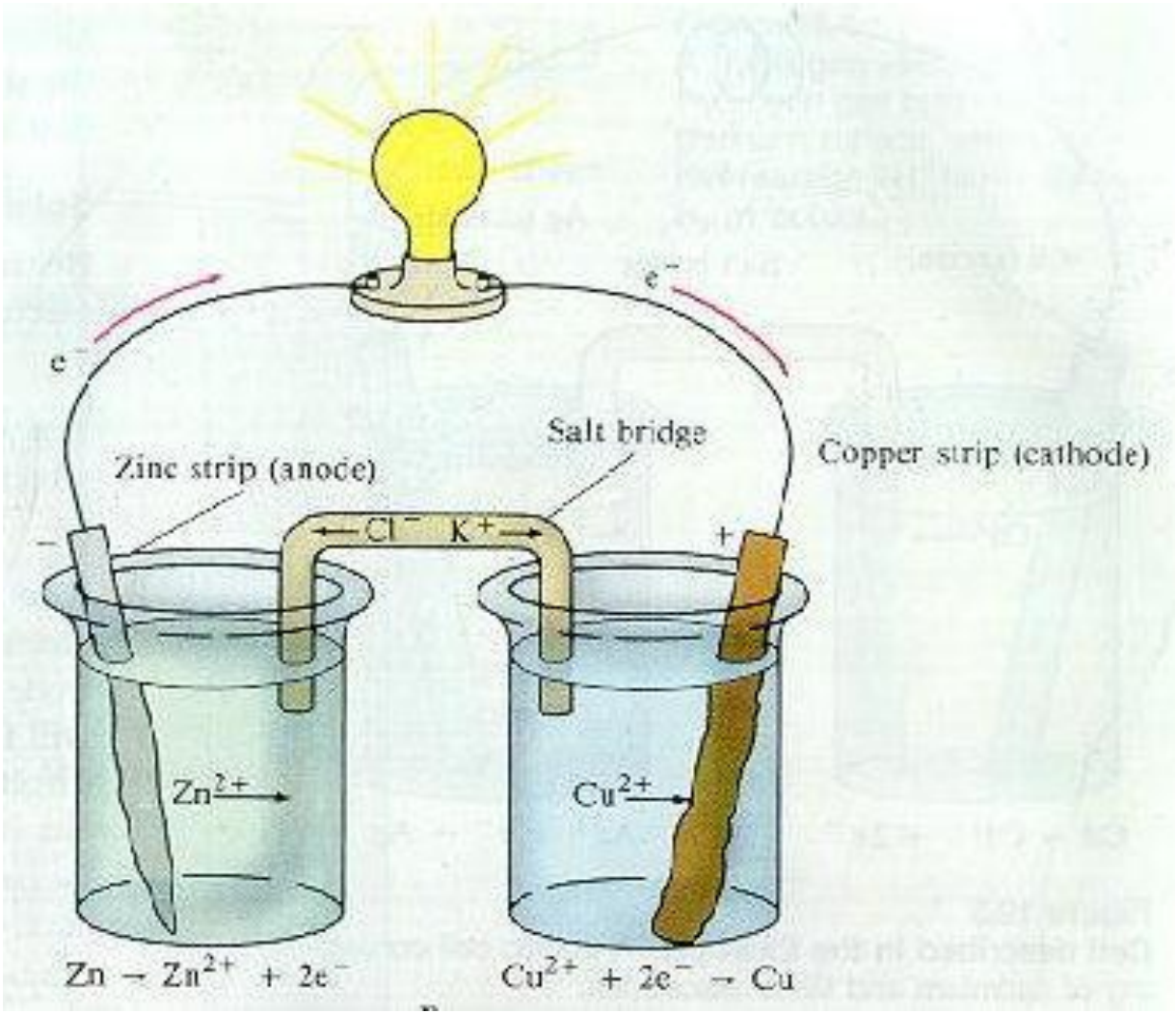


1936г., раскопки в районе Багдада

Механизм возникновения электрического тока в гальваническом элементе



A zink-copper voltaic cell



$$Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$$

$Zn(s)\,|\,Zn^{2+}(aq)$ $\|$ $Cu^{2+}(aq)\,|\,Cu(s)$

anode Salt bridge cathode

$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.38
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.41
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.2
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Fe^{3+}(aq) + 3e^- \rightleftharpoons Fe(s)$	−0.04
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	0.15
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	0.16
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34
$IO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons I^-(aq) + 2OH^-(aq)$	0.49
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	0.52
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	0.77
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	0.80
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	0.80
$Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg(l)$	0.85
$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$	0.90
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	0.90
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	1.07
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49

Стандартный электродный потенциал (восстановления) в водной среде при 25^0C

$$Zn^{2+} + 2e \Leftrightarrow Zn$$

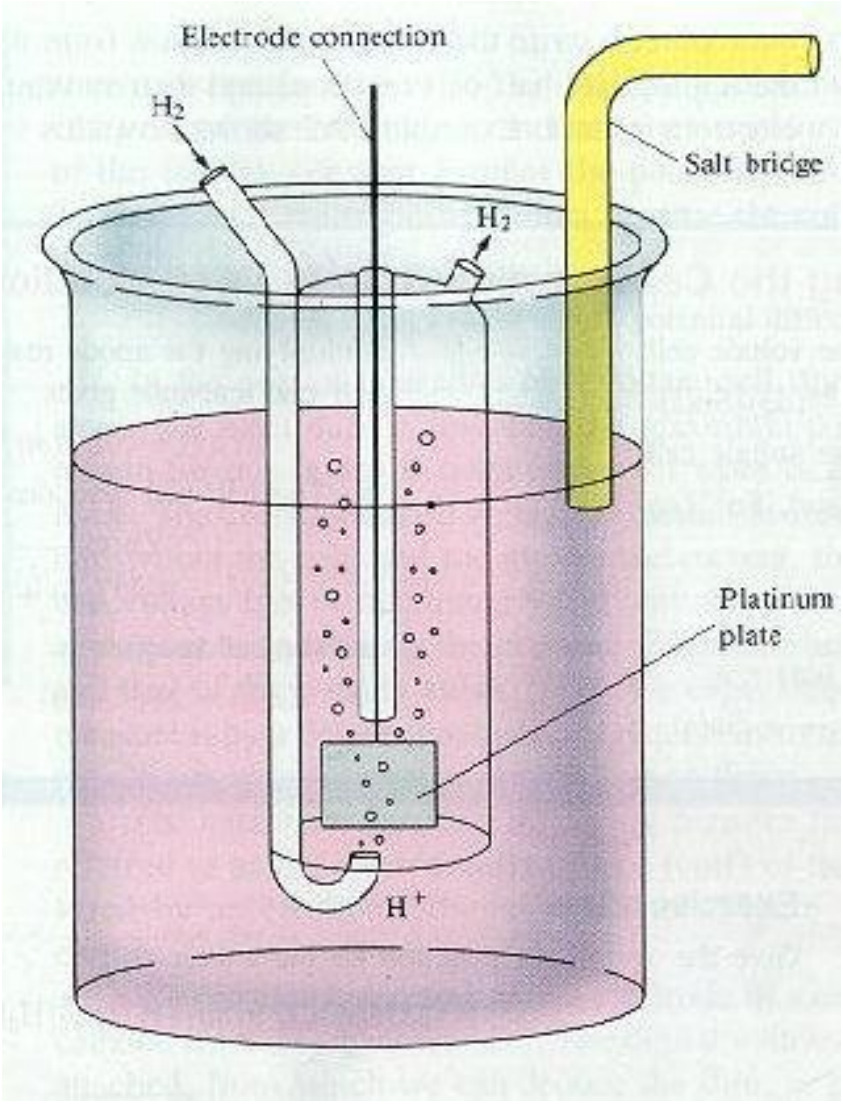
E^0= - 0.76 В

$$E^0_{cell} = E^0_{Ag} - E^0_{Cd}$$

$$Zn(s)\left|Zn^{2+}(aq)\right\|H^+(aq)\left|H_2(g)\right|Pt$$

$$E^0_{Zn} = E^0_{Cathode} - E^0_{anode}$$

$$E^0_{Zn} = -0.76V$$



A hydrogen electrode.

Hydrogen gas bubbles over a platinum surface, where the half-reaction

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

occurs.

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad E^0{}_{Cd} = -0.40V$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E^0{}_{Ag} = 0.80V$$

$$Cd(s) + 2Ag^+(aq) \rightarrow Cd^{2+}(aq) + 2Ag(s) \qquad E^0{}_{Ag} - E^0{}_{Cd} = 1.20V$$

$$Cd(s)\left|Cd^{2+}(aq)\right\|Ag^+(aq)\left|Ag(s)\right.$$

$$Cd^{2+}(aq) + 2Ag(s) \rightarrow Cd(s) + 2Ag^+(aq) \qquad E^0{}_{Cd} - E^0{}_{Ag} = -1.20V$$

$$Ag(s)\left|Ag^+(aq)\right\|Cd^{2+}(aq)\left|Cd(s)\right.$$

Уравнение Нернста

$$\varphi = \varphi^0 + \frac{2.3RT}{zF} \lg \frac{[Ox]}{[\mathrm{Re}\, d]}$$

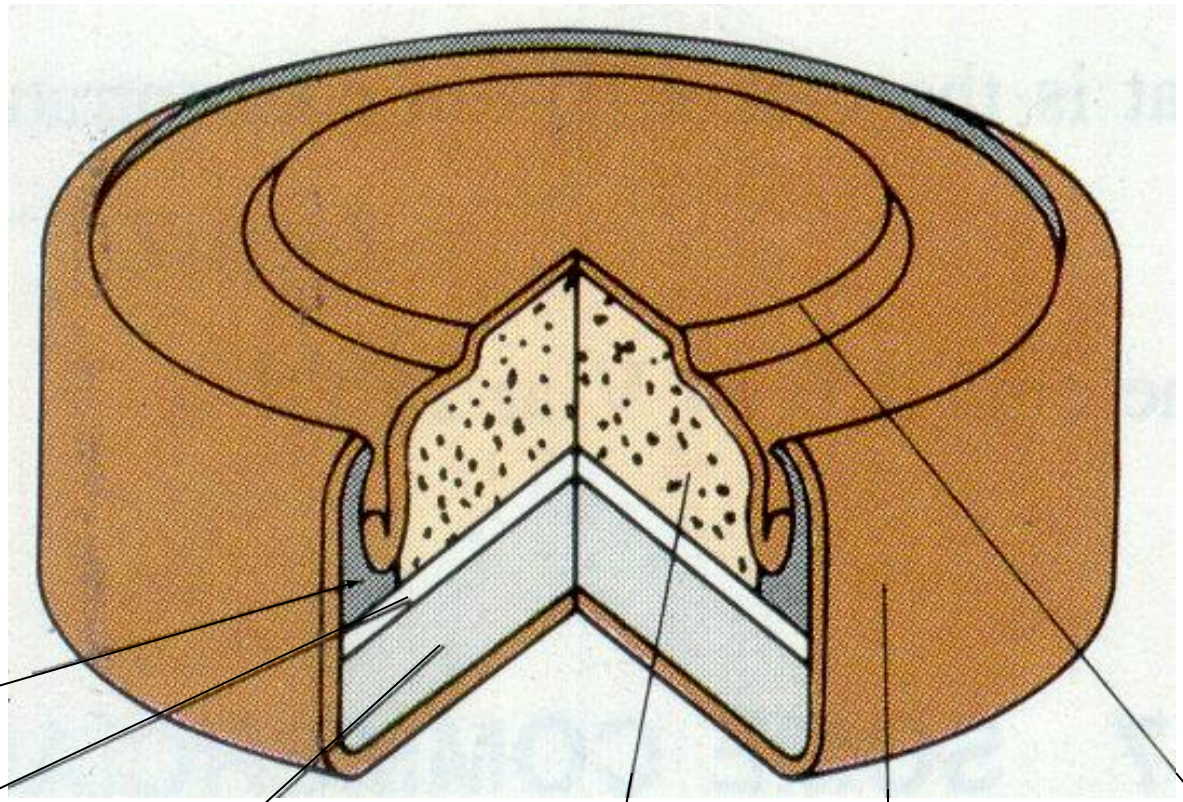
Zn / Zn^{2+} $\quad Zn^{2+} + 2e^- \Leftrightarrow Zn$ $\quad \varphi = \varphi^0 + \frac{0.059}{2} \lg [Zn^{2+}]$

Ag / Ag^{+} $\quad Ag^{+} + e^- \Leftrightarrow Ag$ $\quad \varphi = \varphi^0 + 0.059 \lg [Ag^{+}]$

$Pt / Fe^{2+}, Fe^{3+}$ $\quad Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$ $\quad \varphi = \varphi^0 + 0.059 \lg \frac{[Fe^{3-}]}{[Fe^{2-}]}$

$Pt / MnO^-_4,$ $\quad MnO^-_4 + 8H^+ +$ $\quad \varphi = \varphi^0 + \frac{0.059}{5} \lg \frac{[MnO^-_4][H^+]}{[Mn^{2+}]}$

Mn^{2+}, H^+ $\quad +5e^- \Leftrightarrow Mn^{2+} + 4H_2O$



A small alkaline dry cell. The anode is zinc powder and the cathode is MnO_2, as in the Leclanche cell; however, the electrolyte is KOH.