



**SEMMELWEIS
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Development of Complex Curricula for Molecular Bionics and Infobionics Programs within a consortial* framework**

Consortium leader

PÁZMÁNY PÉTER CATHOLIC UNIVERSITY

Consortium members

SEMMELWEIS UNIVERSITY, DIALOG CAMPUS PUBLISHER

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**Molekuláris bionika és Infobionika Szakok tananyagának komplex fejlesztése konzorciumi keretben

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WORLD OF MOLECULES

(Molekulák világa)

ELECTROCHEMISTRY

(Elektrokémia)

KRISTÓF IVÁN



Previously – Thermodynamics

1. Laws of thermodynamics
2. Chemical thermodynamics
3. Extensive and intensive quantities
4. Heat
5. Entropy
6. Enthalpy
7. Gibbs free energy
8. Equilibrium



Previously - Intensive and extensive quantities
the quotient of two extensives gives an intensive quantity

e.g.
$$\frac{\text{mass (extensive)}}{\text{volume (extensive)}} = \textit{density} \text{ (intensive)}$$

connecting two separate thermodynamic systems with different measures will result in the two systems changing towards a common equilibrium

during this

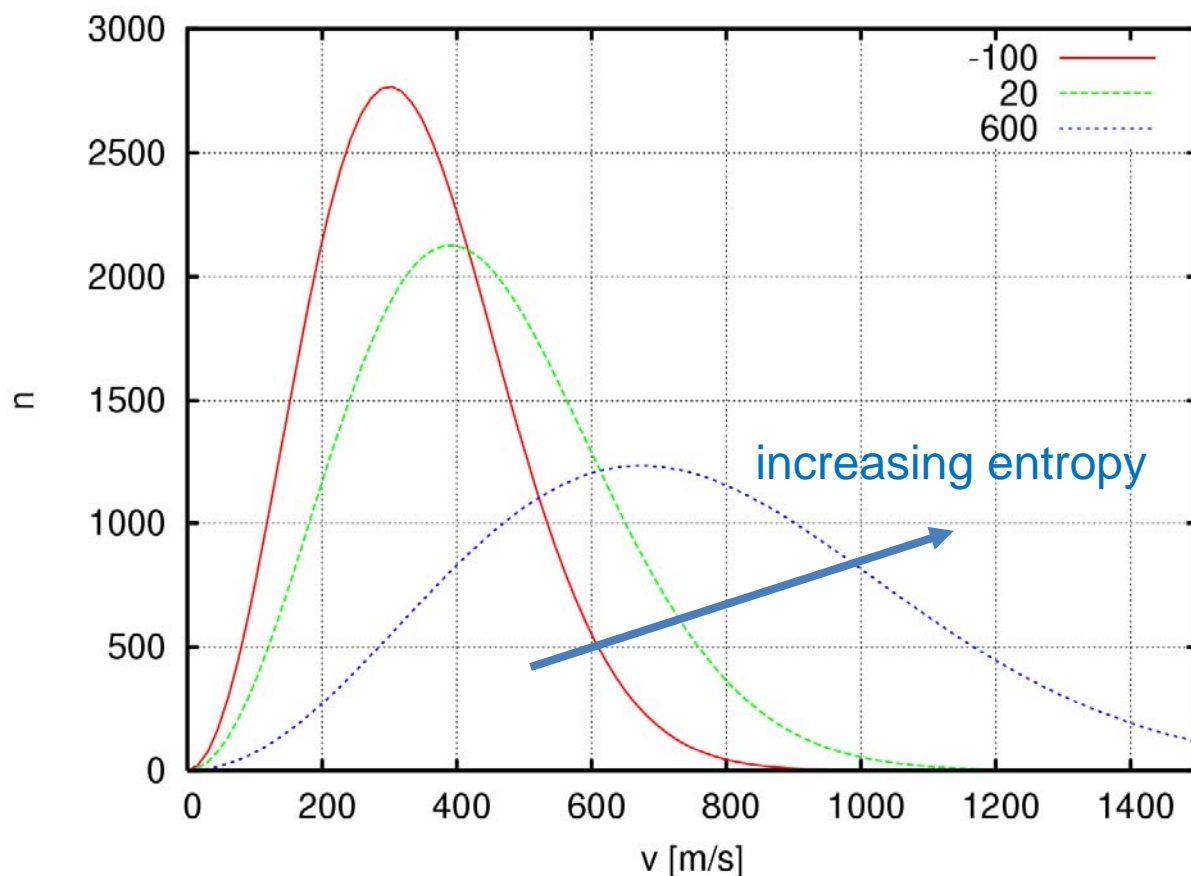
the **extensives** are added

the **intensives equilibrate**





Previously - Maxwell-Boltzmann distribution of molecule speeds



speed distribution of
of 1 million gas
molecules
at -100, 20 and
600 degrees °C

http://it.wikipedia.org/wiki/File:Maxwell-Boltzmann_distribution_1.png

Previously - Gibbs free energy

Gibbs free energy of formation (Δg): the non-mechanical work associated with the formulation of a compound from its elements.

- the chemical potential can be described:

$$\mu_i = \mu_i^0 + RT \ln c_i \quad \mu_i = \mu_i^0 + RT \ln p_i$$

$$\mu_i = \mu_i^0 + RT \ln x_i$$

- the Gibbs free energy of a reaction (similarly to heat of reaction)

$$\Delta G = \underbrace{\sum_i g_{m,i} \cdot n_i}_{\text{products}} - \underbrace{\sum_j g_{m,j} \cdot n_j}_{\text{reactants}}$$



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Electrochemistry

- deals with the changes and transformation of the electric and chemical energy into each other
- usually occurring at a solid-liquid interface
- charge carriers: **electron**: in solids (e.g. metals), or **ion**: in liquids, molten salts
- at the interface of phases there is a change of the type of charge carriers
 - spontaneous: *galvanic cells*
 - forced: *electrolysis*

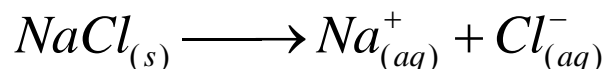




Electrolytes

solutions where there are ions that can move around freely and carry charge

in water: solvated ions, usually solution of acids, bases or salts



solvation occurs because water molecules are dipoles and orient themselves around charged substances

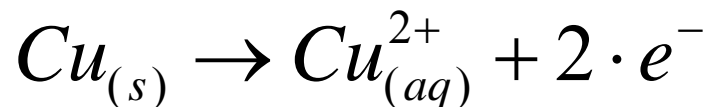
molten salts (have free charge carriers as well)
their descriptor is electrical conductivity



Metal electrode in an electrolyte

if a metal electrode is in an electrolyte containing its ions a redox reaction occurs due to the difference in oxidation states of the same material

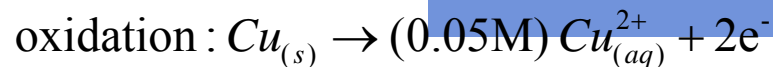
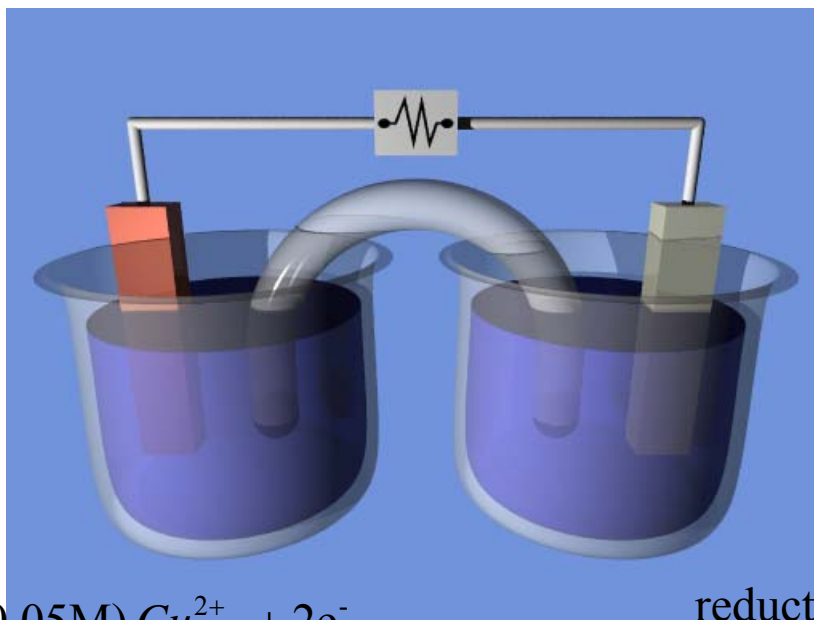
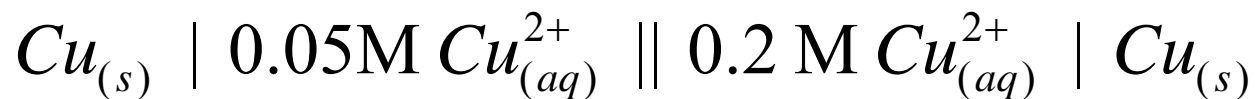
- reduced form \rightarrow oxidized form + $z \cdot e^-$



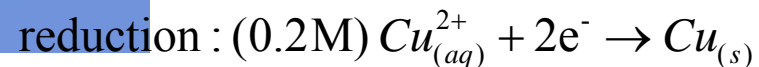
the simplest electrochemical system is a concentration cell, where two electrodes are in contact with their respective solutions

Concentration cell

Cu electrode | 0,05M CuSO₄ || 0,2M CuSO₄ | Cu electrode



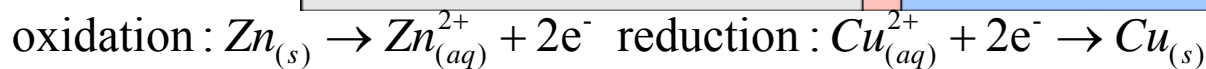
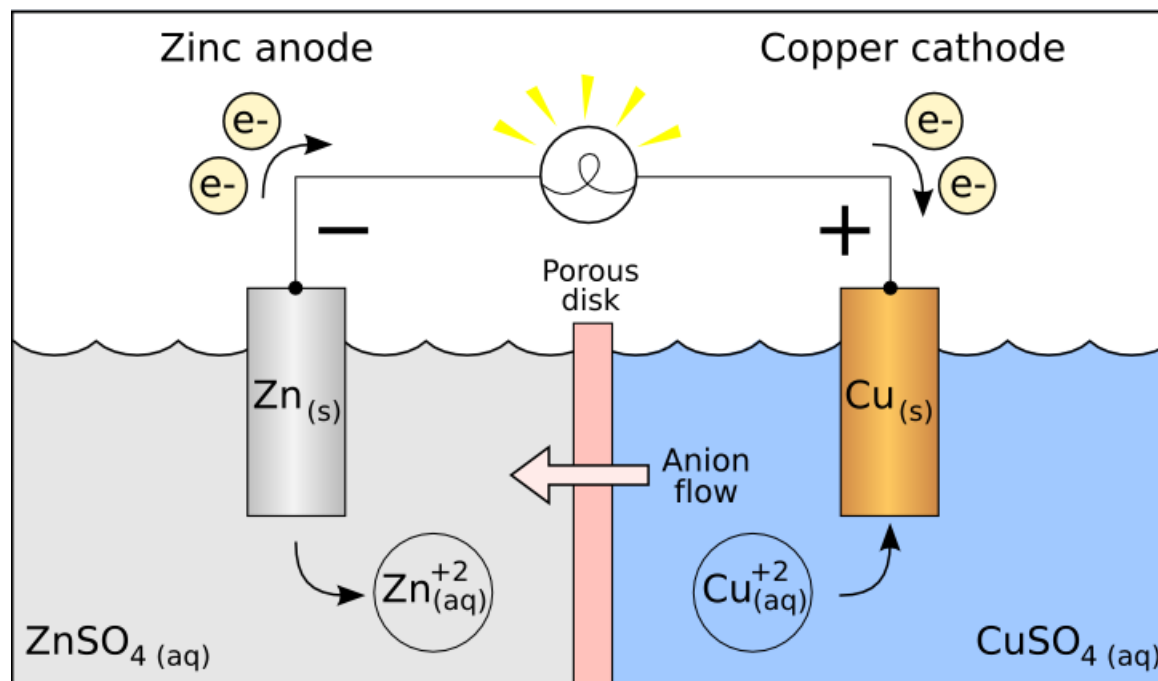
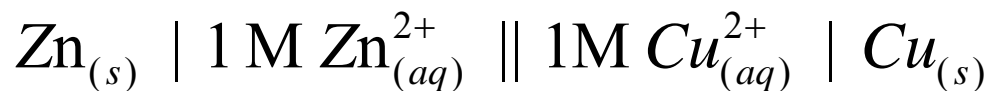
anodic dissolution of the electrode



cathodic deposition of metal copper

<http://it.wikipedia.org/wiki/File:ElectrochemCell.png>

Galvanic cell

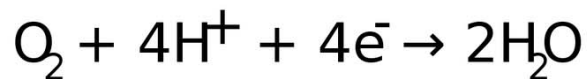
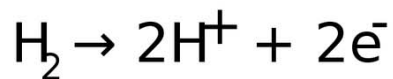
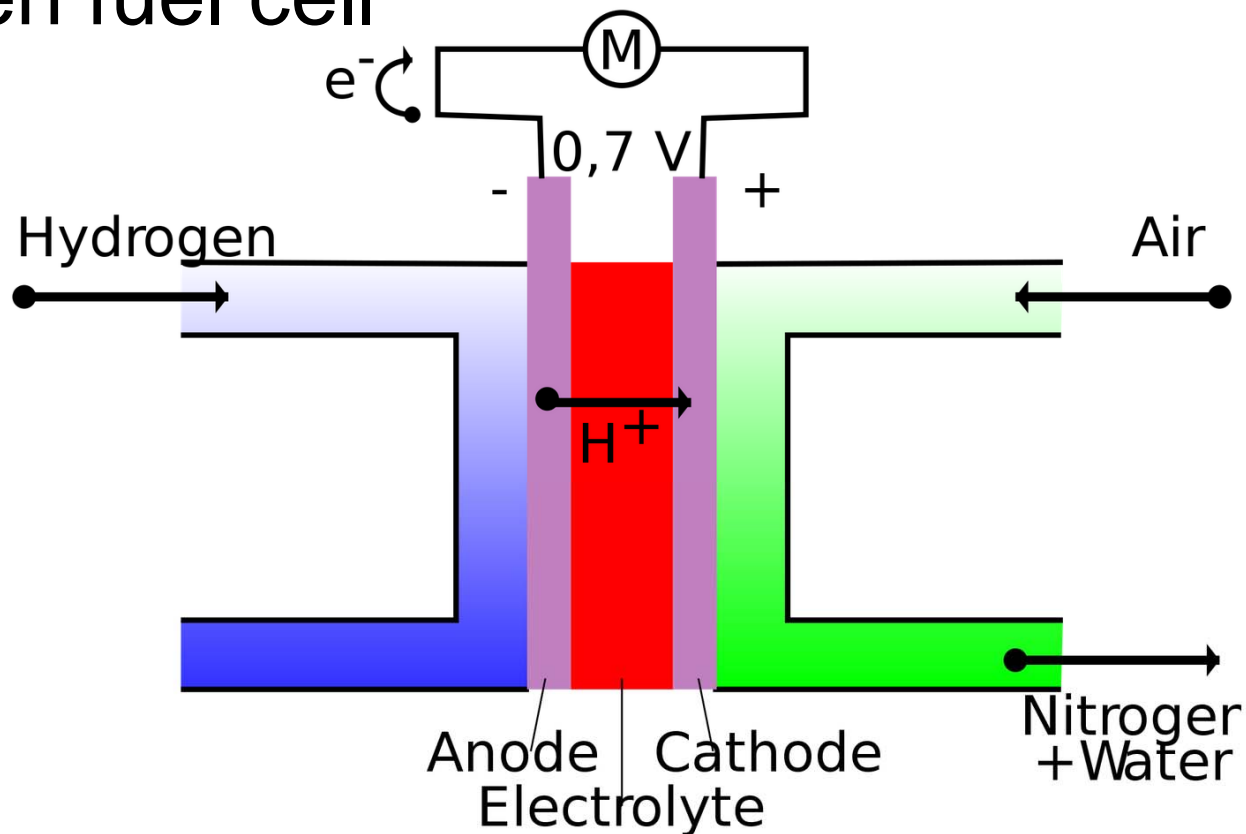


ANODE

CATHODE

http://en.wikipedia.org/wiki/File:Galvanic_cell_with_no_cation_flow.png

Hydrogen fuel cell



http://commons.wikimedia.org/wiki/File:Fuel_cell_EN.svg

Electromotive force

Electrode potentials

- if the electron is not removed from the electrode surface it would result in a local electron excess on the anode and Zn^{2+} excess in the solution
- this results in an electrochemical double layer which generates a potential difference
- on the cathode the lack of electrons and the excess of sulphate ions (SO_4^{2-}) creates a double layer
- these two connected will generate the electromotive force, described by the Nernst equation

$$\varepsilon = \varepsilon_0 + \frac{RT}{zF} \ln c_i$$

$$\varepsilon = \varepsilon_0 + \frac{0,059}{z} \log c_i$$

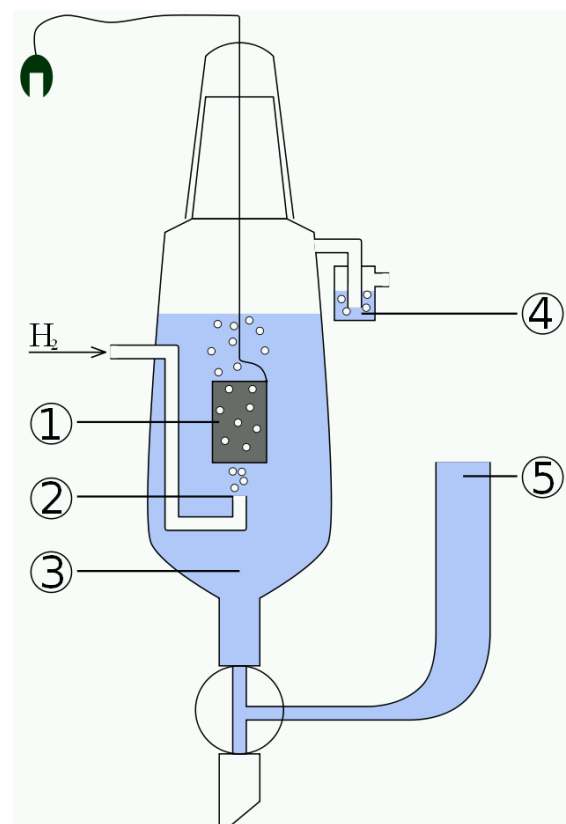
Standard Hydrogen electrode (SHE) - reference

1. Pt electrode
2. H₂ gas
3. acid, where [H⁺]=1 mol/l
4. hydroseal
5. place for counter electrode



$$\varepsilon_0 = 0$$

$$\varepsilon = 0,059 \cdot \log [H^{+}]$$



http://en.wikipedia.org/wiki/File:Standard_hydrogen_electrode_2009-02-06.svg

Standard electrode potentials

| Half-reaction | E° (V) ^[note 1] |
|----------------------------------------------------------------------------------------------------------|-----------------------------------|
| $3/2\text{N}_2(g) + \text{H}^+ + e^- \rightleftharpoons \text{HN}_3(aq)$ | -3.09 |
| $\text{Li}^+ + e^- \rightleftharpoons \text{Li}(s)$ | -3.0401 |
| $\text{N}_2(g) + 4\text{H}_2\text{O} + 2e^- \rightleftharpoons 2\text{NH}_2\text{OH}(aq) + 2\text{OH}^-$ | -3.04 |
| $\text{Cs}^+ + e^- \rightleftharpoons \text{Cs}(s)$ | -3.026 |
| $\text{Rb}^+ + e^- \rightleftharpoons \text{Rb}(s)$ | -2.98 |
| $\text{K}^+ + e^- \rightleftharpoons \text{K}(s)$ | -2.931 |
| $\text{Ba}^{2+} + 2e^- \rightleftharpoons \text{Ba}(s)$ | -2.912 |
| $\text{La}(\text{OH})_3(s) + 3e^- \rightleftharpoons \text{La}(s) + 3\text{OH}^-$ | -2.90 |
| $\text{Sr}^{2+} + 2e^- \rightleftharpoons \text{Sr}(s)$ | -2.899 |
| $\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}(s)$ | -2.868 |
| $\text{Eu}^{2+} + 2e^- \rightleftharpoons \text{Eu}(s)$ | -2.812 |
| $\text{Ra}^{2+} + 2e^- \rightleftharpoons \text{Ra}(s)$ | -2.8 |
| $\text{Na}^+ + e^- \rightleftharpoons \text{Na}(s)$ | -2.71 |
| $\text{La}^{3+} + 3e^- \rightleftharpoons \text{La}(s)$ | -2.379 |
| $\text{Y}^{3+} + 3e^- \rightleftharpoons \text{Y}(s)$ | -2.372 |
| $\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}(s)$ | -2.372 |

Standard electrode potentials

| | |
|---------------------------------------------------------------------------------------------------------|---------------|
| $\text{CO}_2(g) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{HCOOH}(aq)$ | -0.11 |
| $\text{Se}(s) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{Se}(g)$ | -0.11 |
| $\text{CO}_2(g) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}$ | -0.11 |
| $\text{SnO}(s) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{Sn}(s) + \text{H}_2\text{O}$ | -0.10 |
| $\text{SnO}_2(s) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{SnO}(s) + \text{H}_2\text{O}$ | -0.09 |
| $\text{WO}_3(aq) + 6\text{H}^+ + 6e^- \rightleftharpoons \text{W}(s) + 3\text{H}_2\text{O}$ | -0.09 |
| $\text{P}(\text{white}) + 3\text{H}^+ + 3e^- \rightleftharpoons \text{PH}_3(g)$ | -0.063 |
| $\text{HCOOH}(aq) + 2\text{H}^+ + 2e^- \rightleftharpoons \text{HCHO}(aq) + \text{H}_2\text{O}$ | -0.03 |
| $2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2(g)$ | 0.0000 |
| $\text{AgBr}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Br}^-$ | +0.07133 |
| $\text{S}_4\text{O}_6^{2-} + 2e^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$ | +0.08 |
| $\text{Fe}_3\text{O}_4(s) + 8\text{H}^+ + 8e^- \rightleftharpoons 3\text{Fe}(s) + 4\text{H}_2\text{O}$ | +0.085 |
| $\text{N}_2(g) + 2\text{H}_2\text{O} + 6\text{H}^+ + 6e^- \rightleftharpoons 2\text{NH}_4\text{OH}(aq)$ | +0.092 |
| $\text{HgO}(s) + \text{H}_2\text{O} + 2e^- \rightleftharpoons \text{Hg}(l) + 2\text{OH}^-$ | +0.0977 |
| $\text{Cu}(\text{NH}_3)_4^{2+} + e^- \rightleftharpoons \text{Cu}(\text{NH}_3)_2^+ + 2\text{NH}_3$ | +0.10 |
| $\text{Ru}(\text{NH}_3)_6^{3+} + e^- \rightleftharpoons \text{Ru}(\text{NH}_3)_6^{2+}$ | +0.10 |

Standard electrode potentials

| | |
|-----------------------------------------------------------------------------------------------------------------------|--------|
| $\text{Ag}_2\text{O}_3(\text{s}) + 6\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{Ag}^+ + 3\text{H}_2\text{O}$ | +1.67 |
| $\text{HClO}_2(\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HClO}(\text{aq}) + \text{H}_2\text{O}$ | +1.67 |
| $\text{Pb}^{4+} + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}$ | +1.69 |
| $\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$ | +1.70 |
| $\text{AgO}(\text{s}) + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{Ag}^+ + \text{H}_2\text{O}$ | +1.77 |
| $\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$ | +1.78 |
| $\text{Co}^{3+} + \text{e}^- \rightleftharpoons \text{Co}^{2+}$ | +1.82 |
| $\text{Au}^+ + \text{e}^- \rightleftharpoons \text{Au}(\text{s})$ | +1.83 |
| $\text{BrO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{BrO}_3^- + \text{H}_2\text{O}$ | +1.85 |
| $\text{Ag}^{2+} + \text{e}^- \rightleftharpoons \text{Ag}^+$ | +1.98 |
| $\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$ | +2.010 |
| $\text{O}_3(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{O}_2(\text{g}) + \text{H}_2\text{O}$ | +2.075 |
| $\text{HMnO}_4^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}$ | +2.09 |
| $\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-$ | +2.87 |
| $\text{F}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{HF}(\text{aq})$ | +3.05 |

Electromotive force

The electromotive force is calculated from the anodic and cathodic standard electrode potentials taking into consideration the concentrations of the species

$$E = \varepsilon_1^+ - \varepsilon_2^-$$

e.g. for the Galvanic cell

$$E = \varepsilon_{\text{Cu}}^+ - \varepsilon_{\text{Zn}}^- = 0,36\text{V} - (-0,76\text{V}) = 1,12\text{V}$$

$$\varepsilon = \varepsilon_0 + \frac{RT}{zF} \ln c_i$$

$$\varepsilon = \varepsilon_0 + \frac{0,059}{z} \log c_i$$

Redox reactions

redox potential

- similar to the standard electrode potential but both species are in ionic form

$$\Delta G = \mu_{ox} - \mu_{red} = z \cdot F \cdot \varepsilon, \quad \text{és } \mu = \mu_0 + RT \ln c_i$$

$$\mu_{0,ox} + RT \ln c_{ox} - \mu_{0,red} - RT \ln c_{red} = z \cdot F \cdot \varepsilon$$

$$\varepsilon = \frac{\mu_{0,ox} - \mu_{0,red}}{z \cdot F} + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}} = \varepsilon_0 + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}}$$

- the Nernst equation for redox reactions

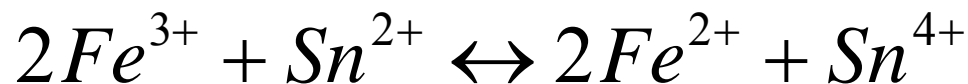
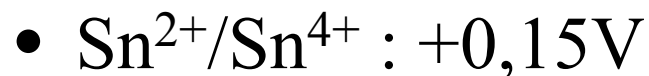
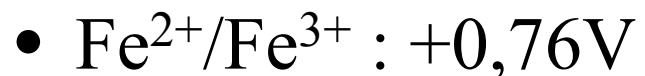
$$\varepsilon = \varepsilon_0 + \frac{0,059}{z} \log \frac{c_{ox}}{c_{red}}$$



Redox reactions

list of redox potentials

e.g.

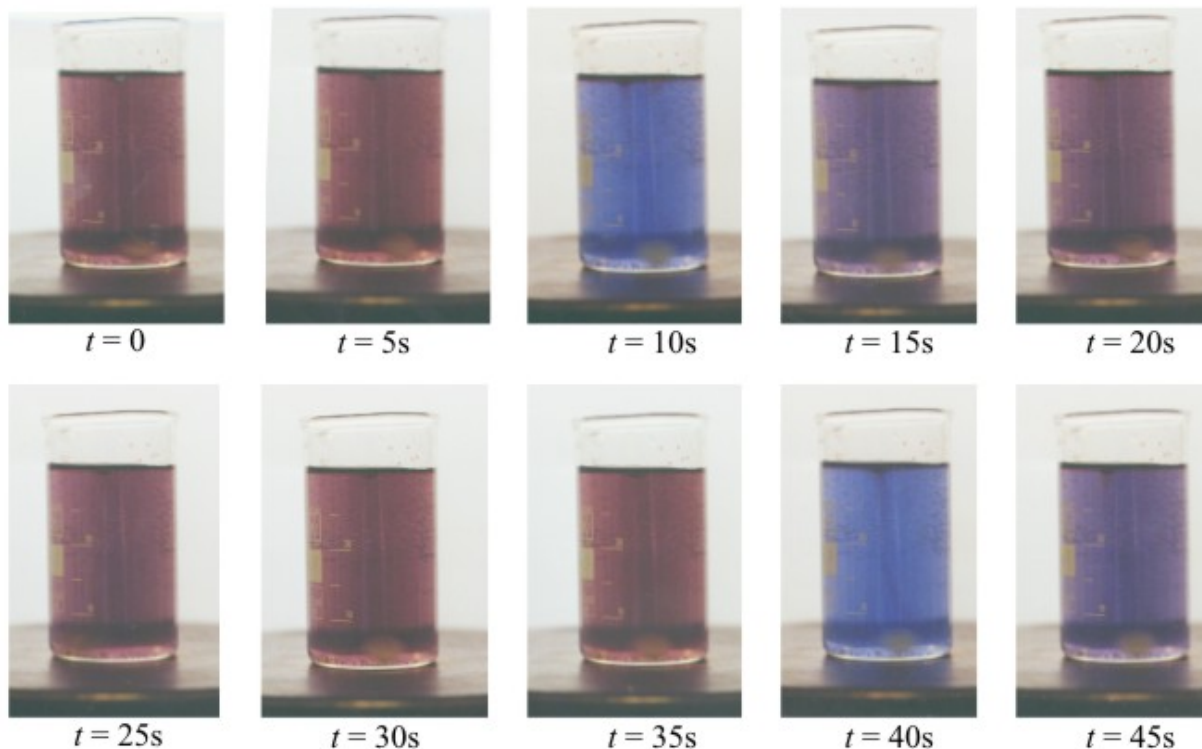


spontaneous →

The higher the redox potential of a system
the more oxidizing the process it comprises

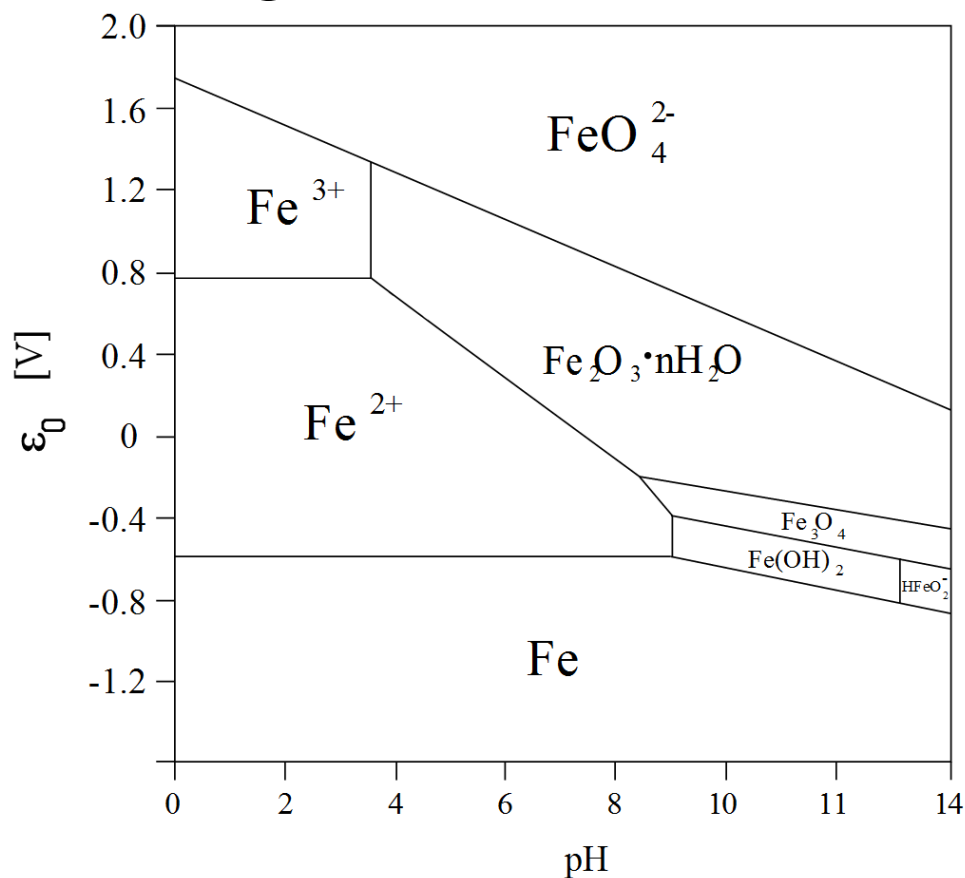


Exotic redox reactions – Belousov-Zhabotinskii oscillating reaction



http://en.wikipedia.org/wiki/File:Bzr_fotos.jpg

Pourbaix diagram ($E - \text{pH}$)



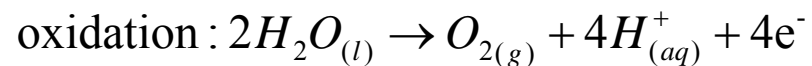
ϵ_0 compared to the standard hydrogen electrode, at room temperature, assuming 1 M solution

http://en.wikipedia.org/wiki/File:Pourbaix_Diagram_of_Iron.svg

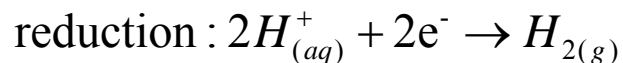
Electrolysis

- with the utilization of external force (electric current) the non-spontaneous reaction occurs in the system
- usually performed in an electrolytic cell
- aim: to separate elements
- e.g. molten salt electrolysis of $\text{NaCl} \rightarrow \text{Na}, \text{Cl}_2$ or water electrolysis to obtain H_2, O_2
- Faraday's law of electrolysis:
$$n = \frac{I \cdot t}{z \cdot F} \quad m = \frac{I \cdot t}{F} \cdot \frac{M}{z}$$
- we have to apply higher potential difference than the standard electrode potential of the system for the electrolysis to occur (*overpotential*)

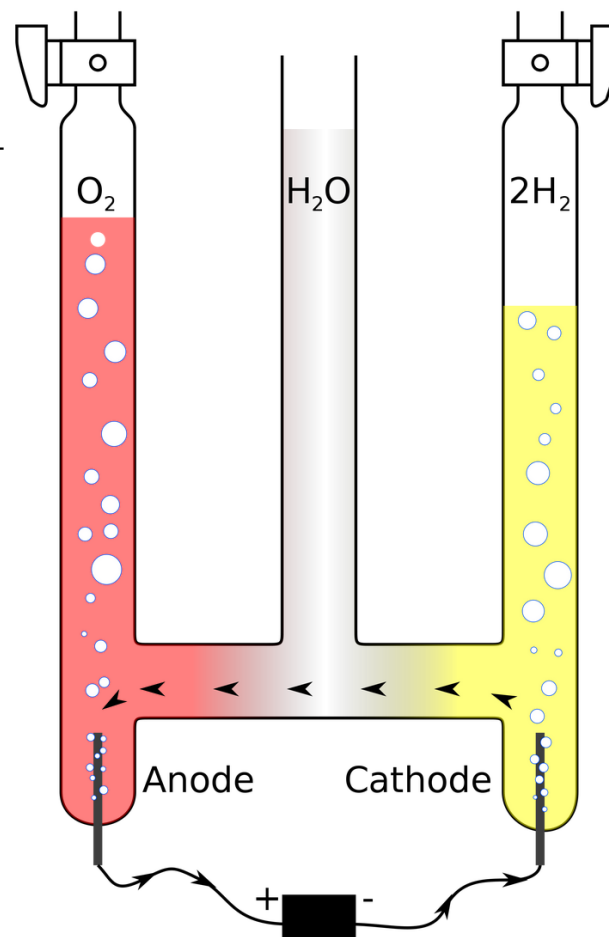
Electrolytic cell



ANODE



CATHODE



http://commons.wikimedia.org/wiki/File:Hofmann_voltameter_fr.svg



Electrolyzing current - Butler – Volmer – Erdey-Grúz equation

the current density can be expressed using the cathodic and anodic current densities:

$$j = nF c_{red}^s k_{ox}^0 e^{\alpha \frac{nF}{RT} E} - nF c_{ox}^s k_{red}^0 e^{-\beta \frac{nF}{RT} E}$$

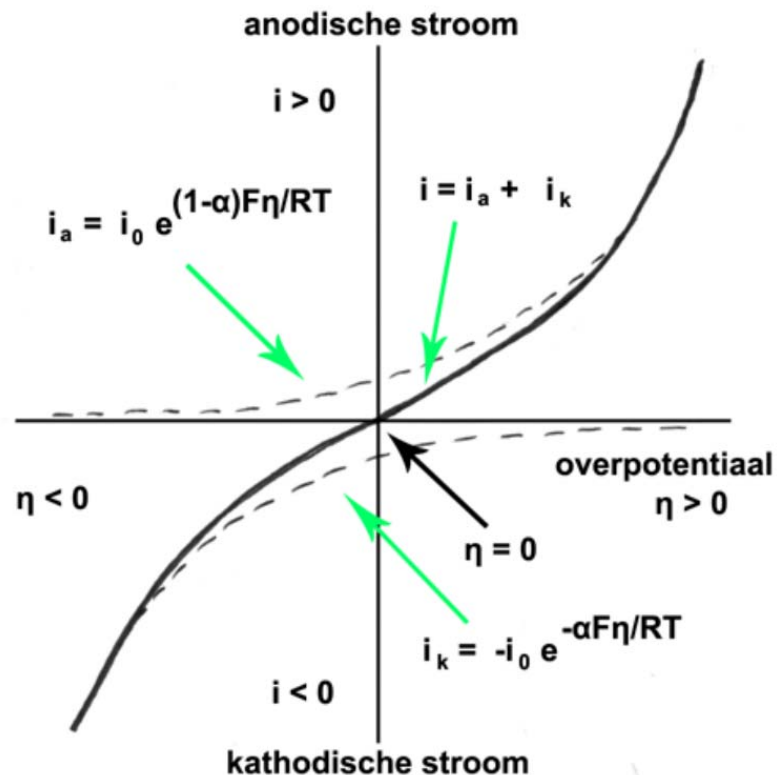
substituting the j_0 exchange current density

$$j_0 = j_a = j_k \quad \text{if} \quad E - E_0 = 0$$

$$j = j_0 \left(e^{\alpha \frac{nF}{RT} (E - E_0)} - e^{-\beta \frac{nF}{RT} (E - E_0)} \right)$$

Electrolyzing current - Butler – Volmer – Erdey-Grúz equation

It describes how the electrical current on an electrode depends on the electrode potential, considering that both a cathodic and an anodic reaction occur on the same electrode



http://en.wikipedia.org/wiki/File:Butler_volmer_equation_graph_nl.png