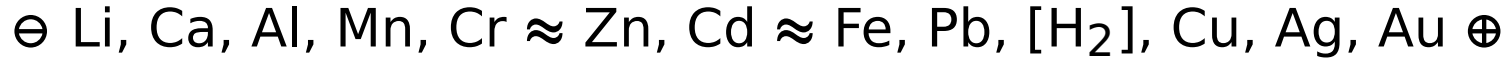


Galvanic series (Beketov, cca 1860):

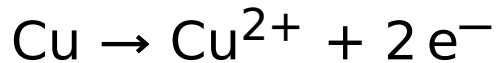


Cell = system composed of two electrodes and an electrolyte.

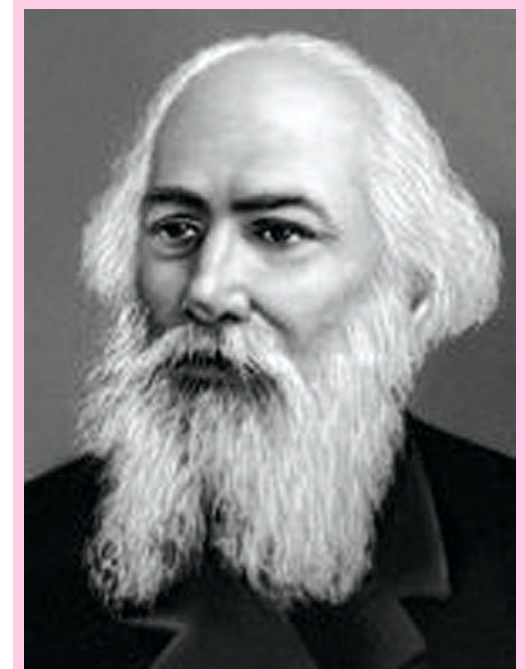
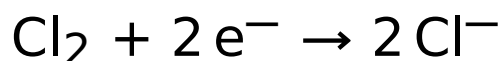
- electrolytic cell: electric energy \rightarrow chemical reaction
- galvanic cell: chemical reaction \rightarrow electric energy
- reversible galvanic cell (zero current)

Electrodes

- **anode** = electrode where **oxidation** occurs



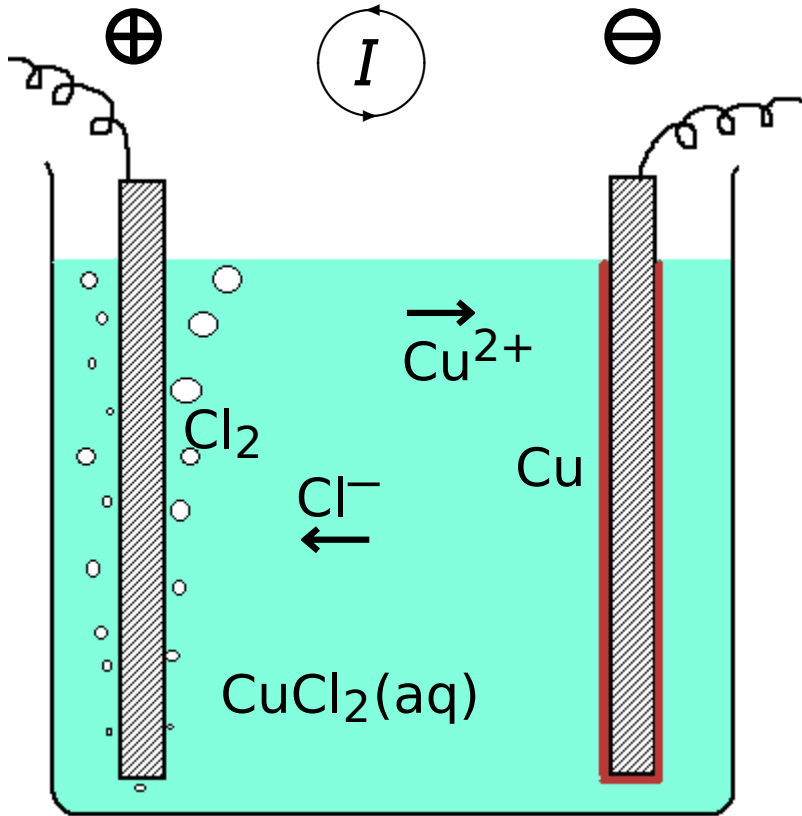
- **cathode** = electrode where **reduction** occurs



credit: Wikipedia (free)

Oxidation and reduction are separated in a cell. The charge flows through the circuit.

electrolytic cell

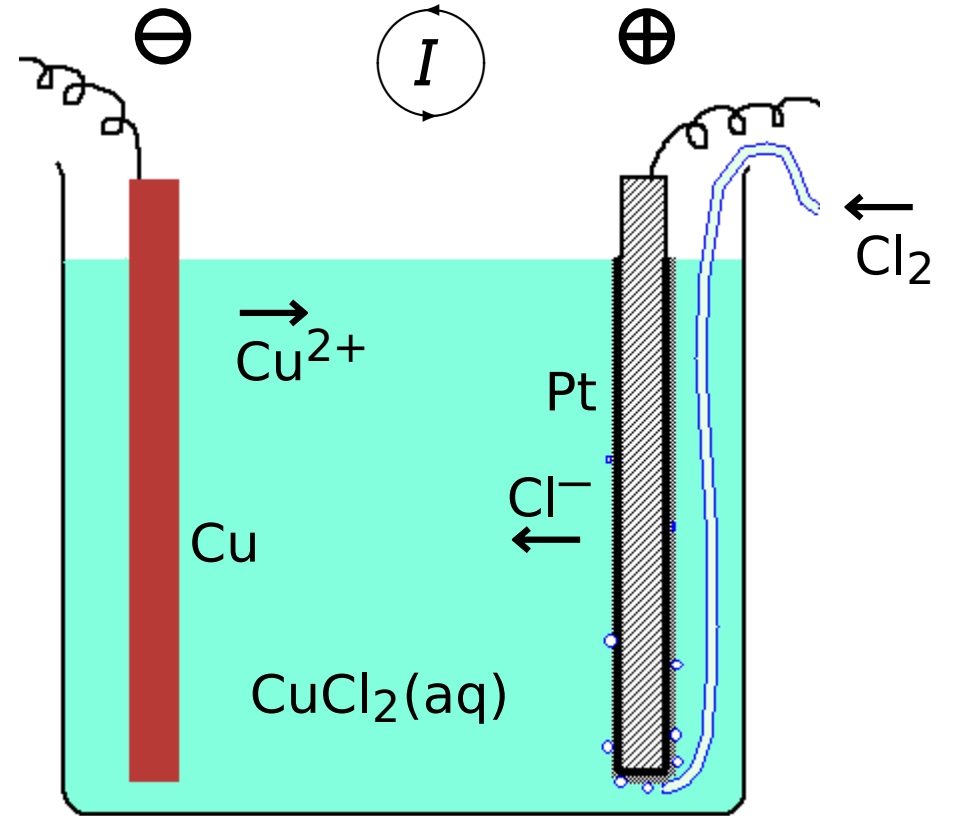


anode

cathode

“anions go to the anode”

galvanic cell



anode

cathode

Electrodes(= half-cells) may be separated by a porous separator, polymeric membrane, salt bridge.

● Cathode \oplus is right (reduction)

● Anode \ominus is left (oxidation)

\ominus negative electrode (anode)

| phase boundary

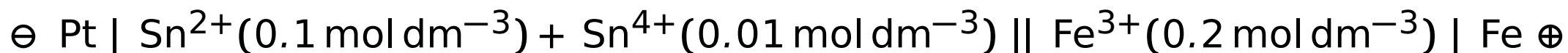
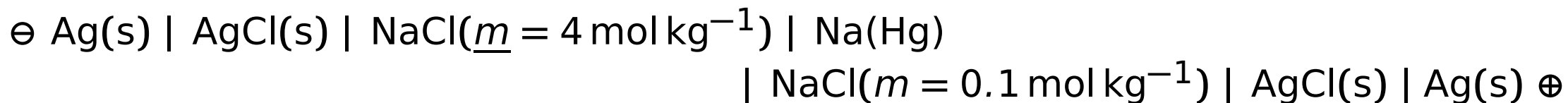
|| salt bridge

\oplus positive electrode (cathode)

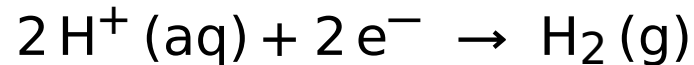
⋮ liquid junction
(porous separator)

⋮⋮ semipermeable membrane

Examples:

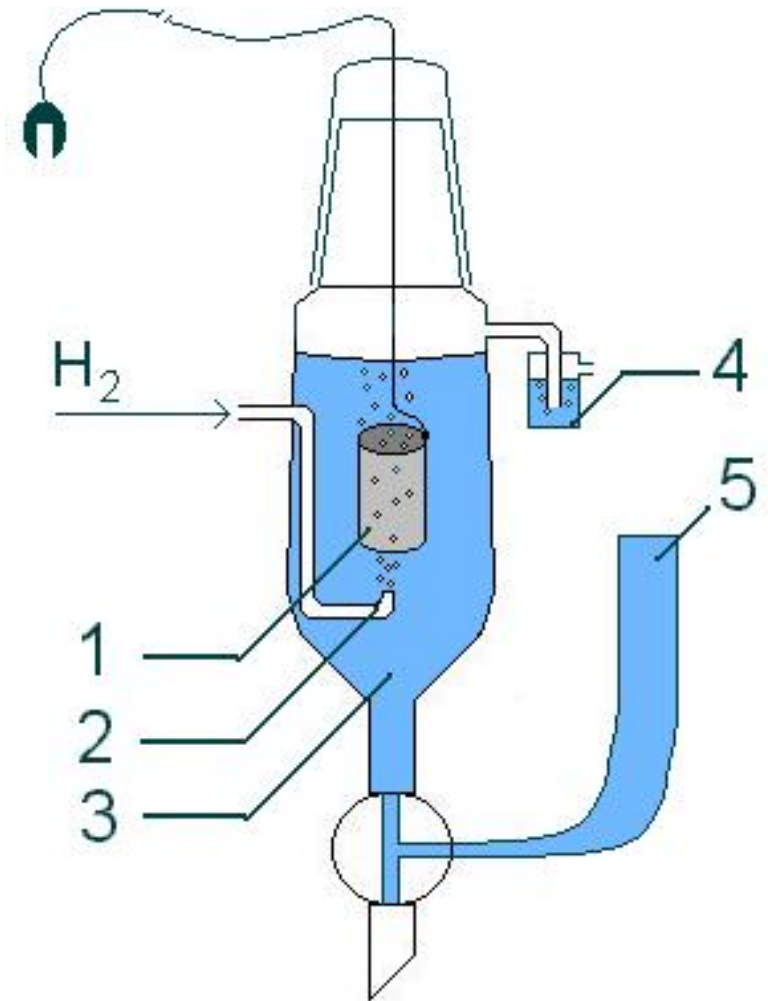


- Also: electromotive potential/voltage, electromotive force (EMF).
- Should be measured at zero-current condition (balanced bridge, sensitive voltmeter)
- Cannot measure a potential of one electrode \Rightarrow zero defined by the **standard hydrogen electrode**:



where $a_{\text{H}^+} = 1$ (pH=0)
and $a_{\text{H}_2} = 1$ ($p_{\text{H}_2} = p^{\text{st}}$).

- **Construction of a hydrogen electrode:**
Pt sheet covered by platinum black, saturated by hydrogen
- symbols: E , \mathcal{E} , $\Delta\phi$; in physics: U



credit: wikipedia

Electrode potential of electrode X = voltage of cell



NB: always the reduction potential

Standard (reduction) potential of an electrode: all reacting compounds have unit activities

Examples: $E_{\text{Cu}^{2+}|\text{Cu}}^{\ominus} = 0.337 \text{ V}$, $E_{\text{Cl}_2|\text{Cl}^-}^{\ominus} = 1.360 \text{ V}$ (at 25 °C)

If the reaction are written in the way the cell produces energy:
reaction = (reduction at cathode) + (oxidation at anode)

$$E = E_{\text{cathode}}^{\text{red}} + E_{\text{anode}}^{\text{ox}}$$

If all reactions are written as a reduction:

reaction = (reduction at cathode) – (reduction at anode)

$$E = E_{\text{cathode}}^{\text{red}} - E_{\text{anode}}^{\text{red}}$$

Reversibility = reactions can be reversed by a small voltage change. No irreversible processes (metal dissolution, diffusion, liquid junction. . .)

$$\Delta_r G_m = W_{el} = -qE = -zFE \quad [p, T]$$

⇒ **Nernst equation:**

$$E = E^\ominus - \frac{RT}{zF} \ln \prod_i a_i^{\nu_i}$$

where $\Delta_r G_m^\ominus = -zFE^\ominus$, $K = \exp[-\Delta_r G_m^\ominus/RT] = \exp[zFE^\ominus/RT]$

$$E^\ominus = E_{\text{cathode}}^{\ominus, \text{red}} + E_{\text{anode}}^{\ominus, \text{ox}} = E_{\text{cathode}}^{\ominus, \text{red}} - E_{\text{anode}}^{\ominus, \text{red}}$$

● $\Delta_r G < 0$ i.e. $E > 0 \Rightarrow$ the cell produces current

$E = 0$ i.e. $\Delta_r G = 0 =$ uncharged cell (equilibrium)

distiguish from: equilibrium potential (at zero current)

● $E_{\text{Cu}^{2+}|\text{Cu}}^\ominus = -E_{\text{Cu}|\text{Cu}^{2+}}^\ominus$ (oxidation) but $E_{\text{Cl}_2|2\text{Cl}^-}^\ominus = E_{\frac{1}{2}\text{Cl}_2|\text{Cl}^-}^\ominus$

● hydrogen electrode right at 25 °C: $E = E_0 - \text{pH} \cdot 0.05916 \text{ V}$

● only electric work W_{el}

● reversible $[p, T]$

$$\Delta_r S_m = - \left(\frac{\partial \Delta_r G_m}{\partial T} \right)_p = zF \left(\frac{\partial E}{\partial T} \right)_p$$

$$\Delta_r H_m = -T^2 \left(\frac{\partial (\Delta_r G_m / T)}{\partial T} \right)_p = zFT^2 \left(\frac{\partial (E/T)}{\partial T} \right)_p$$

$$Q_m = T \Delta_r S_m \quad (\text{II. Law for reversible processes})$$

Oops!

$$\Delta_r U = Q + W = Q - p \Delta_r V + W_{el}$$

\swarrow W_{p-V}

$$\Delta_r H = \Delta_r U + \Delta_r(pV) \stackrel{[p]}{=} \Delta_r U + p \Delta_r V = Q + W_{el}$$

Eq. $Q = \Delta_r H$ holds true only if the only work is pressure-volume

And similarly for standard state ($p = p^{st}$, $a = 1$), e.g.:

$$\Delta_r S_m^\ominus = - \left(\frac{\partial \Delta_r G_m^\ominus}{\partial T} \right)_p = zF \left(\frac{\partial E^\ominus}{\partial T} \right)_p$$

Example.

$$E^\ominus(\text{Cr}^{2+}|\text{Cr}) = -0.913 \text{ V}, E^\ominus(\text{Cr}^{3+}|\text{Cr}) = -0.744 \text{ V}.$$

Calculate $E^\ominus(\text{Cr}^{3+}|\text{Cr}^{2+})$.

Gibbs energies are additive (not potentials)



$$-1F \cdot E^\ominus(\text{Cr}^{3+}|\text{Cr}^{2+}) = -3F \cdot (-0.744 \text{ V}) + 2F \cdot (-0.913 \text{ V})$$

$$E^\ominus(\text{Cr}^{3+}|\text{Cr}^{2+}) = 3 \cdot (-0.744 \text{ V}) - 2 \cdot (-0.913 \text{ V}) = -0.406 \text{ V}$$

- of the first kind (one reaction electrode—ion)
 - cationic, anionic
 - metal, amalgam (metal in Hg), nonmetallic, gas
- of the second kind (nonsoluble salt—two reactions)
- of the third kind
- redox (two oxidation states)
- ion selective (membrane)

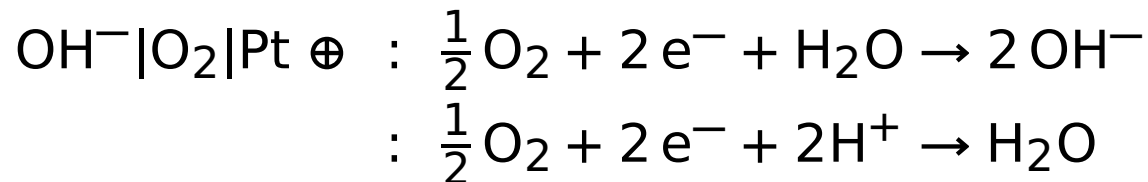
- cationic, metal
ox: $\ominus \text{Zn}|\text{Zn}^{2+}$, red: $\text{Zn}^{2+}|\text{Zn} \oplus$
not for Fe, Al + ions, which are covered by oxides

- amalgam
ox: $\ominus \text{Na}(\text{Hg})|\text{Na}^+$, red: $\text{Na}^+|\text{Na}(\text{Hg}) \oplus$

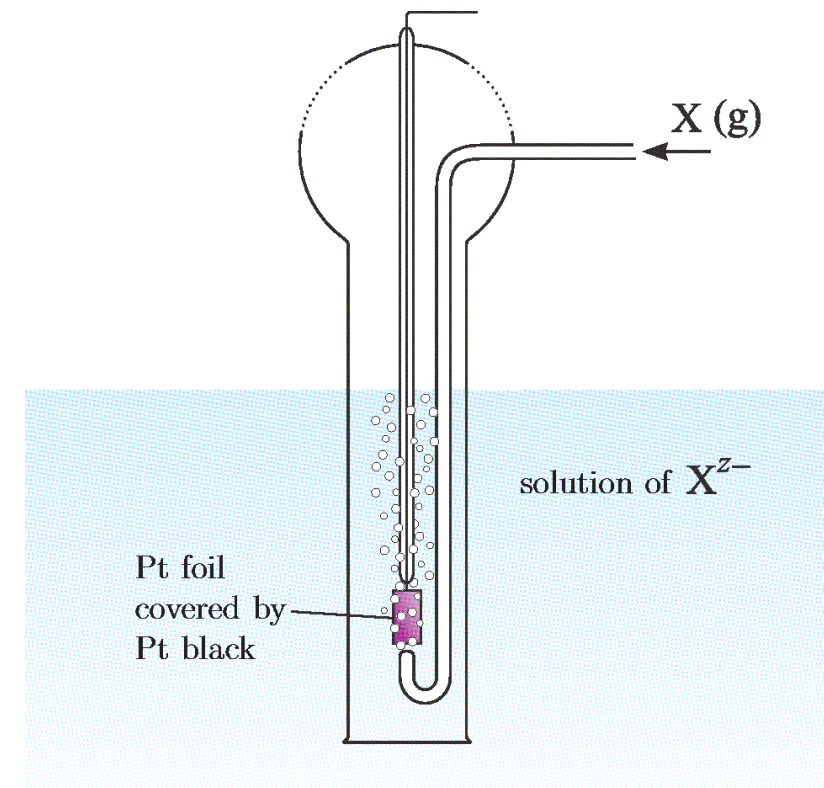
$$E_{\text{Na}^+|\text{Na}} = E_{\text{Na}^+|\text{Na}}^{\ominus} - \frac{RT}{F} \ln \frac{a_{\text{Na}(\text{Hg})}}{a_{\text{Na}^+}}$$

saturated amalgam: $a_{M(\text{Hg})}=1$

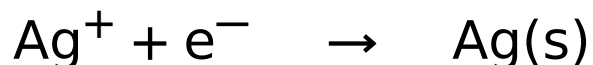
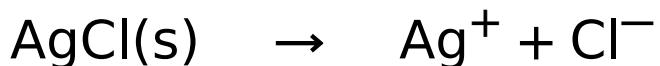
- cationic gas: hydrogen
- anionic gas: chlorine, oxygen \longrightarrow



- similarly: $\text{Br}^-|\text{Br}_2|\text{Pt} \oplus$



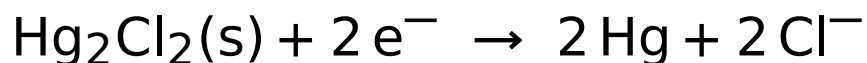
● silver chloride



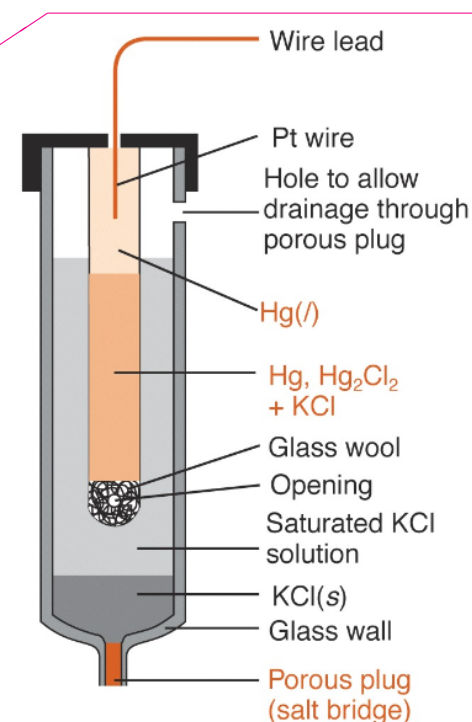
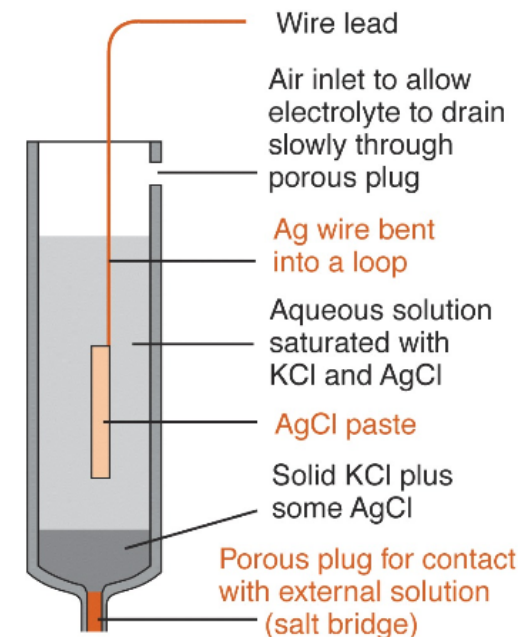
$$E_{\text{AgCl}|\text{Ag}|\text{Cl}^-} = E_{\text{AgCl}|\text{Ag}|\text{Cl}^-}^{\ominus} - \frac{RT}{F} \ln \frac{a_{\text{Ag}} \cdot a_{\text{Cl}^-}}{a_{\text{AgCl}}}$$

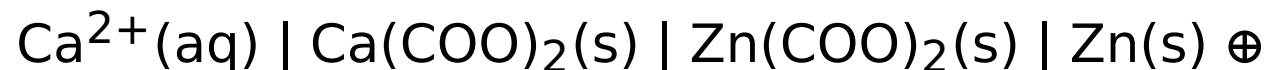
$$= E_{\text{AgCl}|\text{Ag}|\text{Cl}^-}^{\ominus} - \frac{RT}{F} \ln a_{\text{Cl}^-}$$

● mercury chloride (calomel)

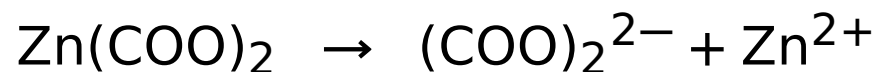
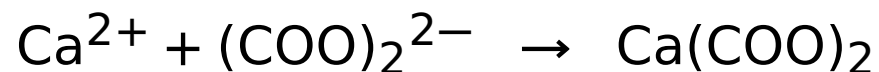


Usage: reference electrodes





Three reactions:

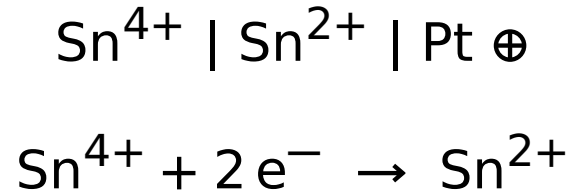


$$E = E^\ominus - \frac{RT}{2F} \ln \frac{1}{a_{\text{Ca}^{2+}}}$$

Can measure $c_{\text{Ca}^{2+}}$ —there is no $\text{Ca} \mid \text{Ca}^{2+}(\text{aq})$ electrode, because Ca reacts with water

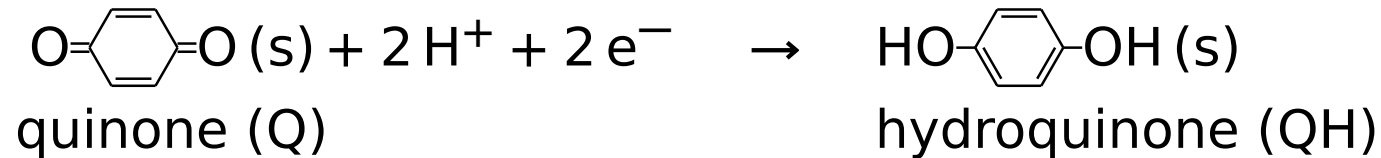
(Ion-selective electrodes are more advantageous)

● metal:



● quinhydrone electrode (pH 1–8):

quinone (p-benzoquinone) + hydroquinone 1:1, sat. \ominus in a buffer



Nernst equation:

$$E_{\text{Q}|\text{QH}} = E_{\text{Q}|\text{QH}}^{\ominus} - \frac{RT}{2F} \ln \frac{a_{\text{QH}}}{a_{\text{Q}} \cdot a_{\text{H}^{+}}^2} = E_{\text{Q}|\text{QH}}^{\ominus} + \frac{RT}{F} \ln a_{\text{H}^{+}}$$

$$\doteq (0.699 - 0.059 \cdot \text{pH}) \text{V}$$

Usage: measuring pH

Semipermeable membrane (for some ions only)

Glass electrode

Membrane of special thin glass permeable for H^+ (and other ions).

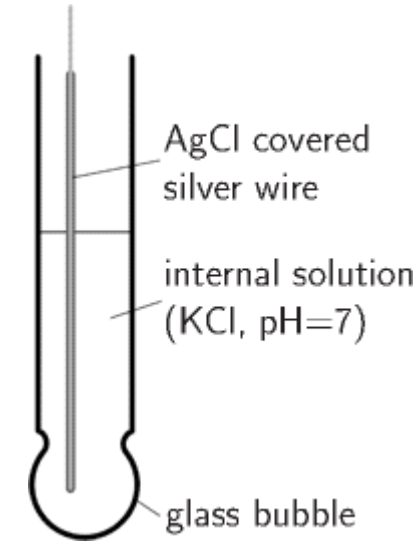
Difference of chem. pot. of both solutions

$$\begin{aligned} &\mu(H^+, \odot) - \mu(H^+, \text{electrode}) \\ &= \frac{1}{RT} \ln \frac{a(H^+, \odot)}{a(H^+, \text{electrode})} \end{aligned}$$

is compensated by the electric work $-FE$. \Rightarrow Nernst equation

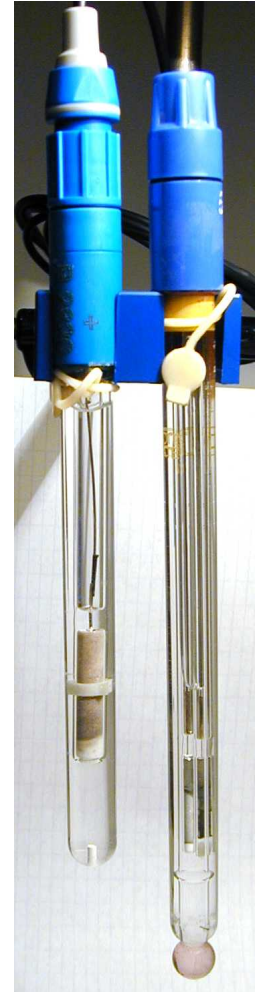
$$E = \text{const} - \frac{RT}{F} \ln a(H^+, \odot) = \text{const} - \frac{RT}{F} \cdot \ln 10 \cdot \text{pH}$$

Usage: measuring pH (2–12), other ions



credit: www.ph-meter.info

ref. silver chloride ↗
glass →



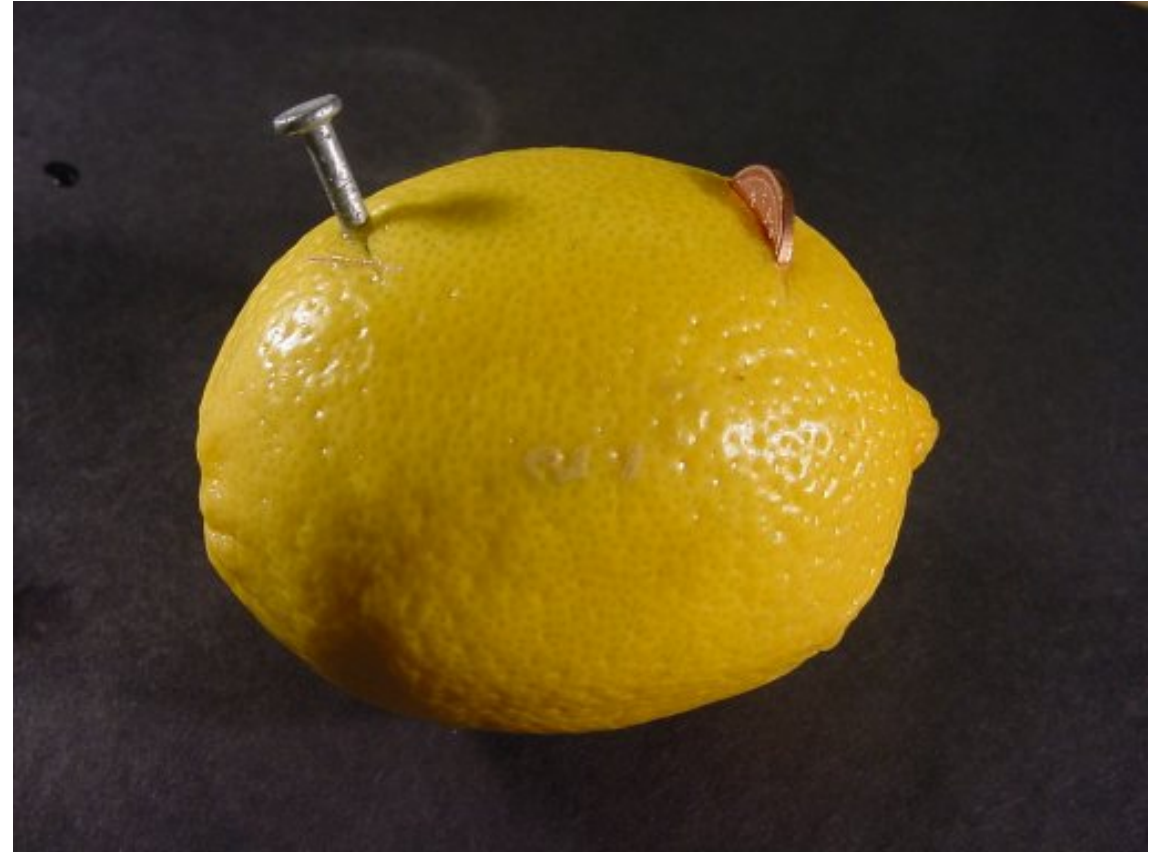
credit: [wikipedia](https://en.wikipedia.org/wiki/Glass_electrode)

By the source of ΔG :

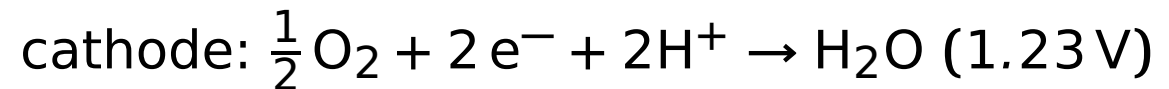
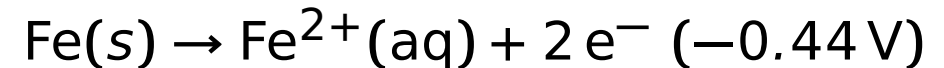
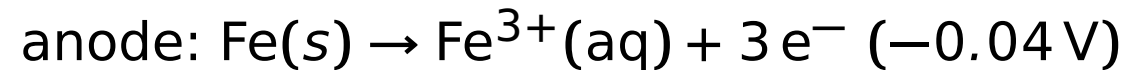
- chemical
- concentration
 - electrolyte
 - electrode

By ion transfer:

- one electrolyte
- with salt bridge
- with membrane



credit: payitoweb.blogspot.com



or reduction of organic
compounds (vitamin C)

Simple chemical cell

● Single electrolyte + electrodes

Example. Consider a Pt electrode saturated by hydrogen and Ag wire covered by AgCl submerged in a solution of HCl ($c = 0.01 \text{ mol dm}^{-3}$) on the top of the highest Czech mountain, Sněžka (1602 m above sea level). The standard reduction potential of the Ag/AgCl/Cl⁻ electrode is 0.222 V ($p^{\text{st}} = 101325 \text{ Pa}$). Calculate the cell voltage. A sea-level-reduced pressure is 999 mbar, temperature 25 °C.

$$p = 83128 \text{ Pa}$$

$$0.4561 \text{ V } (\gamma = 1)$$

$$0.4621 \text{ V (lim. DH)}$$

$$0.4616 \text{ V (DH)}$$



Porous barrier (liquid junction) (:).

Irreversible \Rightarrow liquid junction (diffusion) potential.

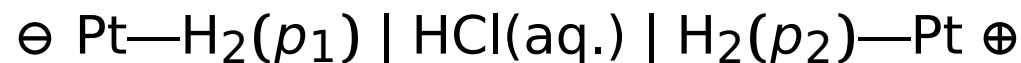
Reduced by the **salt bridge** (||).

Example:

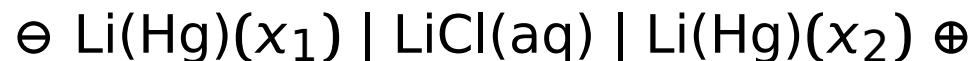


Electrode concentration cell

Examples:



(Given polarity for $p_1 > p_2$)

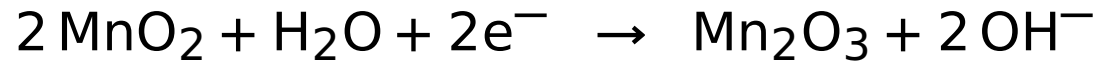


(Given polarity for $x_1 > x_2$)

(One or) more connected cells.

Common disposable batteries:

● Alkaline battery (Zn, MnO_2 + C)



● Lithium (Li metal is light, has high potential)

Electrolyte = salt (e.g., LiBF_4) in organic polar solvent

Several possibilities, e.g.:



- Li-ion, Li-polymer: Li is in C (max. 1 Li in 6 C)



Positive electrode (e.g., in discharged state) LiCoO_2 = layers of CoO_2 intercalated by layers Li^+ . Charging: Li^+ to the solution, $\text{Co}^{\text{III}} \rightarrow \text{Co}^{\text{IV}}$

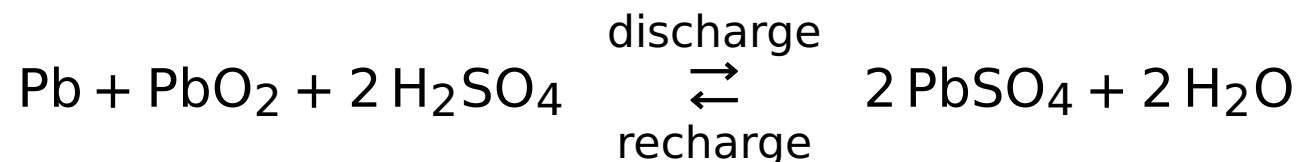
- Ni-MH: hydrogen in metal hydride (M = LaNi_5 , CeAl_5 , TiNi_2 ...)



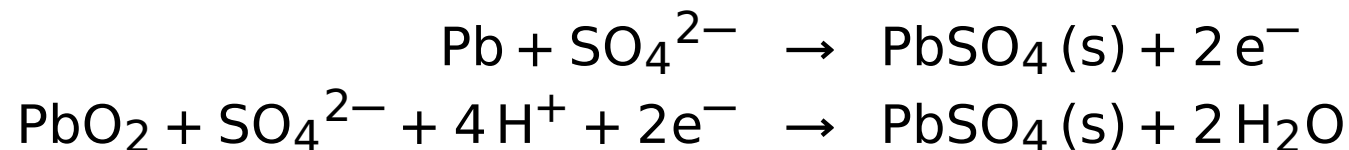
- lead-acid battery (high current)



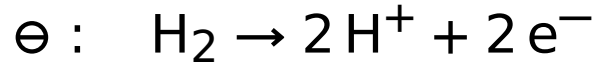
Summary reaction:



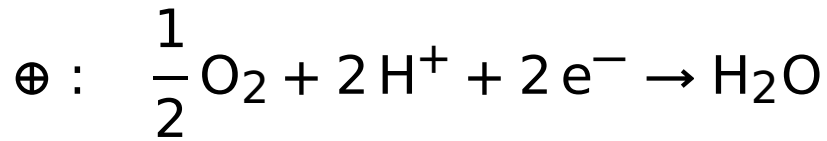
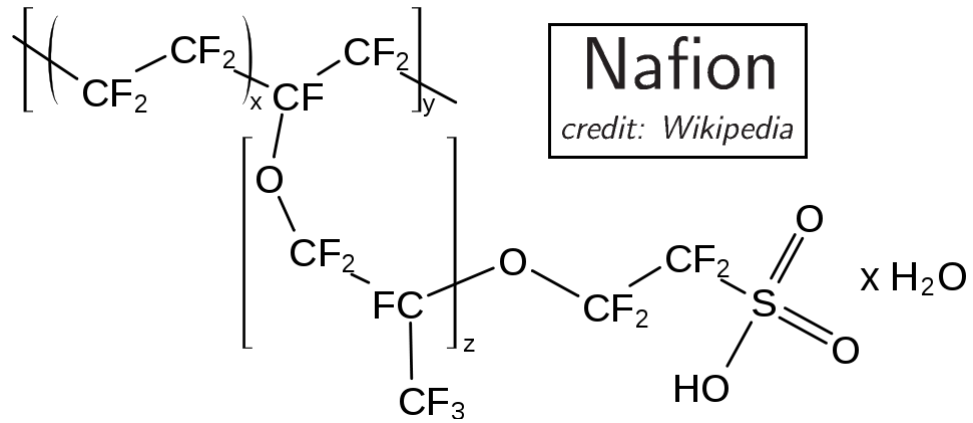
or for anode and cathode:



e.g., oxygen and hydrogen



protons permeate through a membrane



expensive catalysts (Pt)

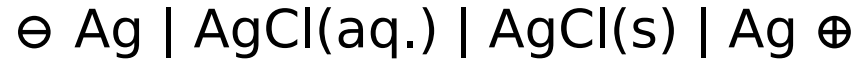
purity of gases (CO)

isopropanol fuel cell



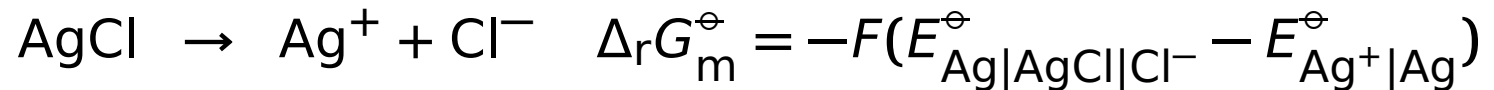
Example. Determine the solubility product of AgCl using the standard potentials at 25 °C.

Data: $E^\ominus(\text{Ag}|\text{Ag}^+) = 0.799 \text{ V}$, $E^\ominus(\text{Ag}|\text{AgCl}|\text{Cl}^-) = 0.222 \text{ V}$.



$$\ominus, \text{ red : } \text{ Ag}^+ + \text{ e}^- \rightarrow \text{ Ag} \quad \Delta_r G_m^\ominus = -F E_{\text{Ag}^+|\text{Ag}}^\ominus \quad \times (-1)$$

$$\oplus, \text{ red : } \text{ AgCl} + \text{ e}^- \rightarrow \text{ Ag} + \text{ Cl}^- \quad \Delta_r G_m^\ominus = -F E_{\text{Ag}|\text{AgCl}|\text{Cl}^-}^\ominus \quad \times (+1)$$



$$K_s = \exp\left(-\frac{\Delta_r G^\ominus}{RT}\right) = \exp\left[\frac{F}{RT} (E_{\text{Ag}|\text{AgCl}|\text{Cl}^-}^\ominus - E_{\text{Ag}^+|\text{Ag}}^\ominus)\right] = 1.76 \times 10^{-10}$$

Short-circuit cell(virtual Ag in \ominus AgCl): the Nernst equation is

$$E = 0 = (E_{\text{Ag}|\text{AgCl}|\text{Cl}^-}^\ominus - E_{\text{Ag}^+|\text{Ag}}^\ominus) - \frac{RT}{F} \ln(a_{\text{Cl}^-} \cdot a_{\text{Ag}^+})$$

= equilibrium condition

$$a_{\text{Cl}^-} \cdot a_{\text{Ag}^+} = K_s$$

Electrode reaction:

1. diffusion of reactants to the electrode,
- (2. reaction in the adjacent layer),
3. adsorption of reactants to the electrode,
4. electron transfer of adsorbed molecules/ions and the electrode,
5. desorption of the products,
- (6. reaction in the adjacent layer),
7. diffusion of products out of the electrode.

In case of slowdown: **polarization of electrodes:**

- concentration polarization (1., 7.)
- chemical polarization

is the voltage needed above the equilibrium potential (at one electrode) for the reaction to be actually observed—a sort of the activation energy.

- Depends on the electrode material
(hydrogen on Pt: small, on Cu: 0.5 V, on Zn: 0.7 V),
- decreases slightly with increasing temperature,
- depends on the current density ($\eta \approx a + b \ln j$),
- ⊖ increases power consumption during electrolysis
- ⊕ high hydrogen overpotential on metals allows electrochemical deposition of metals with (slightly) negative potentials (Cr, Co), lead-acid battery
some compounds catalyze H₂ production, can be used in analysis

- anodic phase: \ominus metal is dissolved
- cathodic phase: \oplus metal is deposited

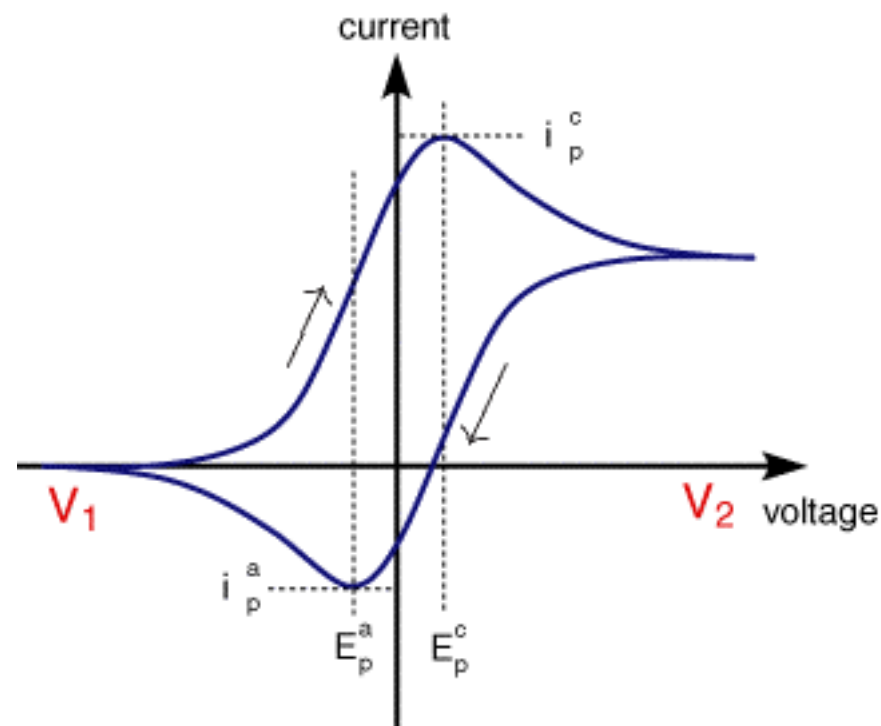
Cathodic protection:

- passive – by anode of a more reactive metal (Zn, Al), which dissolves and produces a negative protective voltage on an object (ship hull) – “sacrificial anode”
- active – additional \ominus voltage on the object, anode is \oplus (large pipes upto 50 V, 50 A)



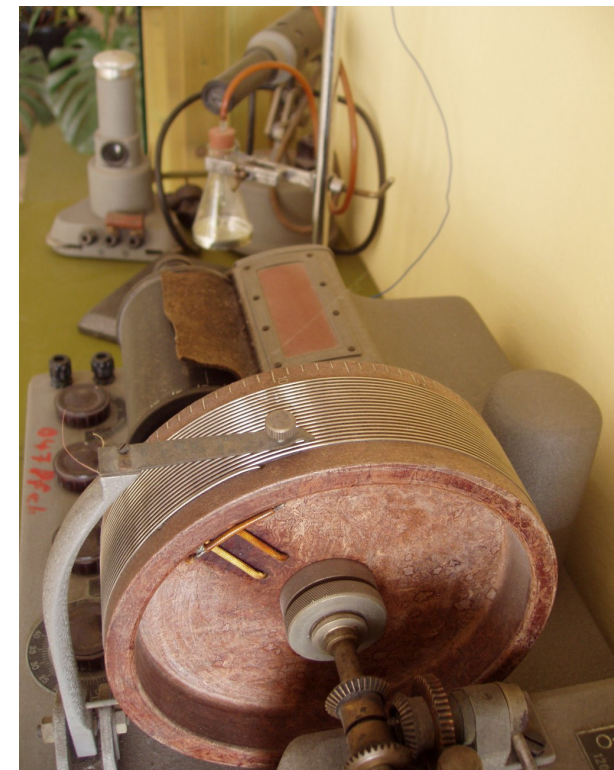
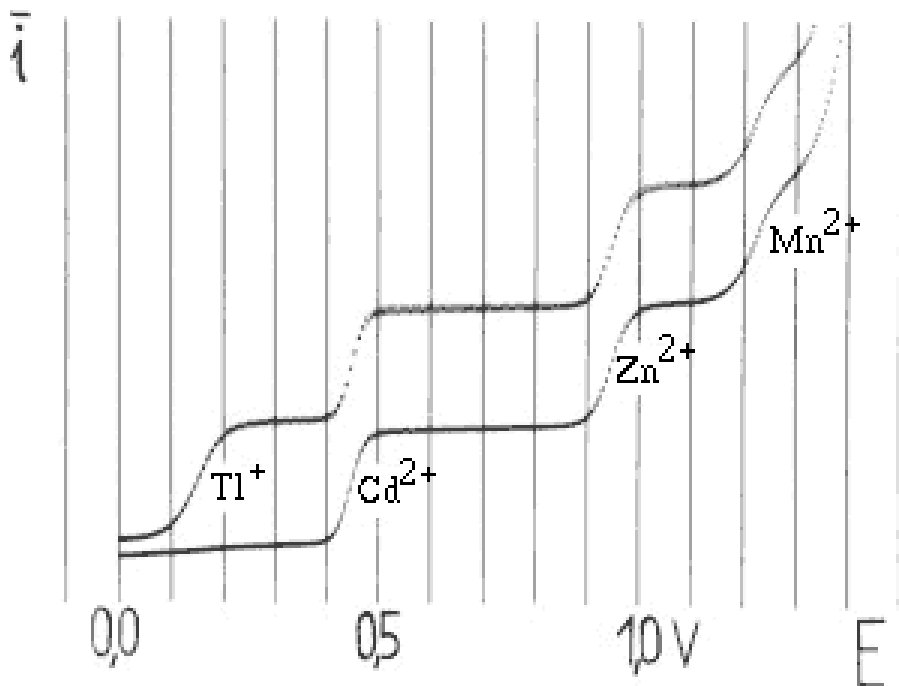
credit: RŠmi Kaupp (Wikimedia Commons)

- coulometry – charge or current needed for a chemical reaction (Faraday's laws of electrolysis; Cu, Ag, O₂+H₂)
 - calibration of ammeters (ampere meters)
 - coulometric titration (const. current, time to equivalence)
- potentiometry – voltage of a cell, (almost) zero current activity (concentration) of a substance is determined, then:
 - pH (glass electrode, quinhydrone, . . .)
 - other ions
 - acidity constants
 - solubility products
 - activity coefficients
 - potentiometric titrations (pH etc.)
- voltammetry – current vs. applied voltage:
 - cyclic voltammetry (right)
 - polarography



Voltammetric technique with a dropping mercury electrode

- Linear E : sensitivity up to $1 \times 10^{-5} \text{ mol dm}^{-3}$
Problem: capacitive current
- Differential pulse polarography (DPP):
sensitivity to $1 \times 10^{-7} \text{ mol dm}^{-3}$



Jaroslav Heyrovský