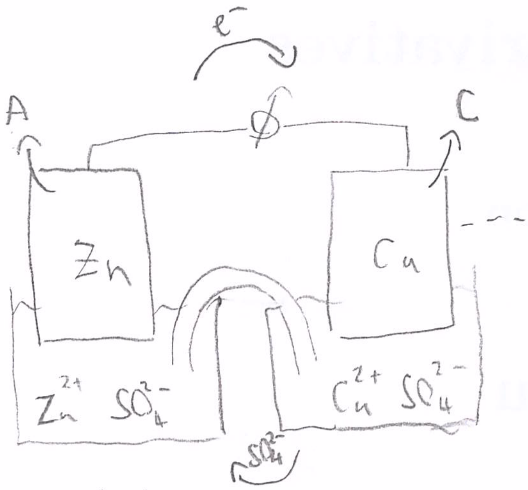
ELECTROCHEMISTRY

galvanic cells

- galv. cell: spontaneous redox reaction
  oxidation and reduction separated in space



phase border   salt bridge

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

aqueous   solid

$\psi_C - \psi_A = E$: electromotive force, $\frac{J}{C} = V$

oxidation   reduction

$\psi_A < \psi_C$

ANODE   CATHODE

in practice we use

$\varepsilon_C - \varepsilon_A = E$

ε: electrode potential
- E of the galv. cell comp. from the electrode and the std. H electrode
- can be comp. from the Nernst eq.

How to use the Nernst eq.?

1, write the half-reaction as if reduction took place:

$Zn^{2+} + 2e^- \rightarrow Zn$ (same num. of electrons as the other half reac.!)

2, substitute into the Nernst eq.

$$\varepsilon = \varepsilon^\circ - \frac{RT}{zF} \ln \frac{\prod_i a_{red,i}^{\nu_i}}{\prod_j a_{ox,j}^{\nu_j}} = \varepsilon^\circ_{Zn/Zn^{2+}} - \frac{RT}{2F} \ln \frac{1}{a_{Zn^{2+}}}$$

z: num. of electrons in the half reaction

only soluted species are considered in the ln!

$a_i = \gamma_i^\pm \cdot \frac{c_i}{c_0}$, $c_0 \equiv 1 \frac{mol}{dm^3}$

$R = 8{,}314 \frac{J}{mol K}$

$F = 96485 \frac{C}{mol}$

$\mathcal{E}^\circ$: std. electrode potential : e. pot. of the std. electrode

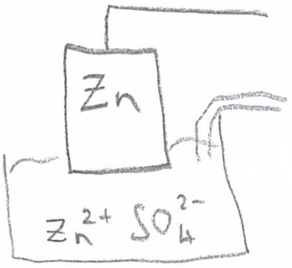
std electrode: $a_i = 1$ for all i in the half reaction

$\mathcal{E}^\circ$ is 0 by definition for $H_2/2H^+$ electrode at every T

$$\boxed{\text{for other electrodes, } \mathcal{E}^\circ_{T_1} \neq \mathcal{E}^\circ_{T_2} \; !}$$

$\mathcal{E}^\circ$ values are measured and tabulated for a given T

METAL ELECTRODES

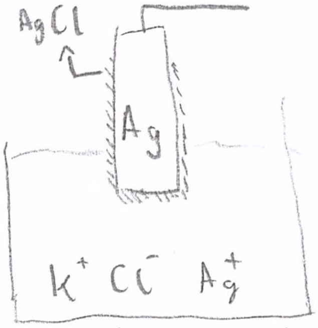


metal dipped into a solution of its own ions : $Zn(s)|Zn^{2+}$

$$\boxed{\mathcal{E}_{Zn/Zn^{2+}} = \mathcal{E}^\circ_{Zn/Zn^{2+}} - \frac{RT}{2F}\ln\frac{1}{a_{Zn^{2+}}}}$$

if $Zn^{2+} + 2e^- \to Zn$ is the reductive half-reaction

METAL - INSOLUBLE SALT ELECTRODES



metal covered with its insoluble salt dipped into a solution containing the union of the salt : $Ag(s)|AgCl(s)|Cl^-$

solubility constant: $L = a_{Ag^+} \cdot a_{Cl^-}$

$$a_{Ag^+} = \frac{L}{a_{Cl^-}}$$

$$\boxed{\mathcal{E}_{Ag+Cl^-/AgCl} = \mathcal{E}^\circ_{Ag+Cl^-/AgCl} - \frac{RT}{F}\ln a_{Cl^-}}$$

if $AgCl + e^- \to Ag + Cl^-$

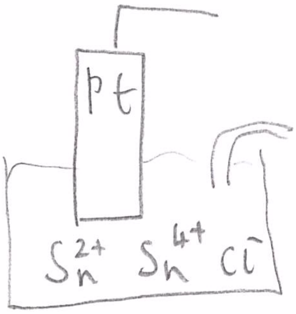
$$\boxed{\mathcal{E}_{Ag/Ag^+} = \mathcal{E}^\circ_{Ag/Ag^+} - \frac{RT}{F}\ln\frac{1}{a_{Ag^+}} = \mathcal{E}^\circ_{Ag/Ag^+} + \frac{RT}{F}\ln L - \frac{RT}{F}\ln a_{Cl^-}}$$

if $Ag^+ + e^- \to Ag$

both refer to the same electrode!

$$\boxed{\ln L = \left(\mathcal{E}^\circ_{Ag+Cl^-/AgCl} - \mathcal{E}^\circ_{Ag/Ag^+}\right) \cdot \frac{zF}{RT}}$$

REDOX ELECTRODE

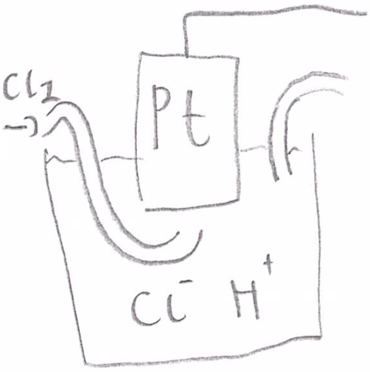


the metal does not take part in the reaction

$$\boxed{\varepsilon_{Sn^{2+}/Sn^{4+}} = \varepsilon^0_{Sn^{2+}/Sn^{4+}} - \frac{RT}{2F}\ln\frac{a_{Sn^{2+}}}{a_{Sn^{4+}}}}$$

if $Sn^{4+}+2e^-\rightarrow Sn^{2+}$

GAS ELECTRODE



indifferent metal dipped into a solution
gas is pumped into it with pressure p

$$\boxed{\varepsilon_{2Cl^-/Cl_2} = \varepsilon^0_{2Cl^-/Cl_2} - \frac{RT}{2F}\ln\frac{a^2_{Cl^-}}{p/p_0}}$$

if $Cl_2+2e^-\rightarrow 2Cl^-$

$p_0 \equiv 1$ bar

gas is not always the oxidized form!
(e.g., $2H^++2e^-\rightarrow H_2$)

THERMODYNAMIC FUNCTIONS OF GALVANIC CELLS

$\Delta_r G = -z\cdot F\cdot E \rightarrow \frac{J}{mol}$

$\Delta_r S = z\cdot F\cdot\left(\frac{\partial E}{\partial T}\right)_{p,T} \rightarrow \frac{J}{mol\,K}$

$\Delta_r H = \Delta_r G + T\Delta_r S \rightarrow \frac{J}{mol}$

CONDUCTIVITY OF ELECTROLYTES

$$\boxed{G = \frac{\varkappa}{C_{cell}}}$$

~ G: conductance, [S]

~ $\varkappa$: conductivity, [S/m]
(or: specific conductance)

~ C_{cell}: cell constant, $[\frac{1}{m}]$
- depends on the shape (geometry) of the container holding the electrolyte
- can be determined experimentally from measuring the G of a cell containing an electrolyte with a known $\varkappa$ (often KCl solution is used)

$$\boxed{\Lambda = \frac{\varkappa}{c}}$$

$$\boxed{c = \frac{\varkappa}{\Lambda}}$$

~ Λ: molar conductivity, $[\frac{Sm^2}{mol}]$
- for diluted solutions we can approximate Λ as

$$\boxed{\Lambda \simeq \Lambda^\infty = \nu_K \lambda_K + \nu_A \lambda_A}$$

- if our solution contains several soluted species: $\Lambda^\infty = \sum_i \Lambda_i^\infty$

~ c: concentration, $\underline{[mol/m^3]}$!!!

~ $$\varkappa = \sum_i \underset{\underset{\text{dissociated fraction!}}{\downarrow}}{[\text{subst.}]} \cdot \Lambda_i^\infty = \sum_j [\text{ion}] \cdot \lambda_j$$