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Electrochemistry

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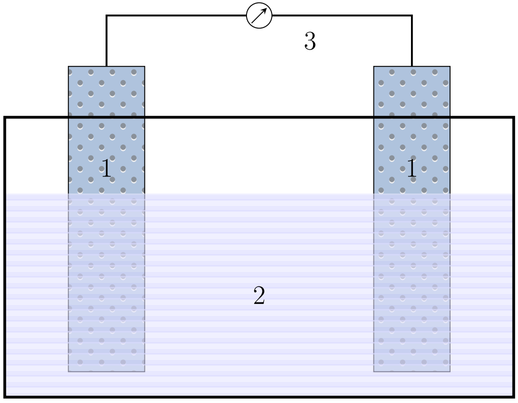
1 Definitions

The basic concepts

- Electrochemical processes are accompanied by a mutual transition of chemical and electrical forms of energy
  - In a *Galvanic element* the chemical energy turns to electrical one
  - In an *Electrolyzer* the electrical energy turns to chemical one
- An *electrochemical system* is the key concept



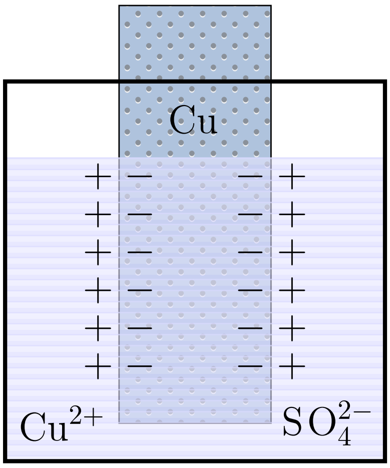
1 – electrodes;
2 – electrolyte solution (or melt);
3 – external circuit.
An external circuit is the conductor of the *first kind*;
Solution (or melt) is the conductor of the *second kind.*

- An *electrode* is the interface between the first and second kind conductors

2 Electrode equilibrium

2.1 Standard electrode potential

- There is double electrical layer on the electrode surface



Copper plate in $CuSO_4$ solution:
the Cu *atoms* are on the plate;
the Cu^{2+} *ions* are in the solution.
An equilibrium establishes on the interface:

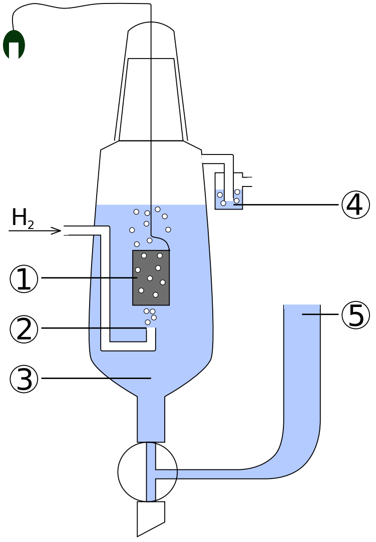
$$Cu^{2+} + 2e \rightleftarrows Cu^0$$

The *electrode potential* E establishes on the electrode due to this equilibrium.

- Standard electrode potential $E°$ is related to the standard conditions ($T = 298$ K, $P = 101.3$ kPa, concentration of ion is 1 mol/L)
- The chemical activity of metal is determined by its $E°$!

2.2 Standard hydrogen reference electrode

- The standard potential of $2H^+ + 2e \rightleftarrows H_2$ system is taken equal to 0.000 Volts exactly



Standard hydrogen electrode (S.H.E.) scheme:

1. Platinized platinum electrode,
2. Hydrogen gas bubbles,
3. Acid solution with $a(H^+) = 1$ mol/L,
4. Hydroseal for prevention of oxygen interference,
5. Reservoir via which the second electrode should be attached. The connection can be direct (through a narrow tube), or through a salt bridge.

- For the metal electrodes $M^{n+} + ne \rightleftarrows M$ it defines the so-called *metal activity series*: for example: $E^\circ(Zn^{2+}/Zn) = -0.76$ V, so zinc is more active than hydrogen, $E^\circ(Cu^{2+}/Cu) = +0.34$ V, so copper is less active

2.3 Nernst equation

- *Nernst equation* determines a potential (E) of the system:
$$\mathrm{Ox} + ne \rightleftarrows \mathrm{Red}$$
depending on conditions (T, c)
$$E(Ox/Red) = E^\circ(Ox/Red) - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]}, \text{ where:}$$
  - n is the number of electrons in electrode process;
  - $F = eN_A = 96485$ Coul/mol is Faraday constant;
  - $\frac{[Red]}{[Ox]} = K_{eq}$ is the electrode equlibrium constant.

- Nernst equation form at $T = 298$ K:
$$E = E^\circ + \ln 10 \cdot \frac{RT}{nF}\lg\frac{[Ox]}{[Red]} = E^\circ + \frac{0.05916}{n}\lg\frac{[Ox]}{[Red]}$$
  - For example: $MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$
  - $E = E^\circ + \frac{0.05916}{5}\lg\frac{a(MnO_4^-)a^8(H^+)}{a(Mn^{2+})}, \quad E^\circ = 1.51$ V
  - so, it's clear that pH influences the oxidizing properties of the anions

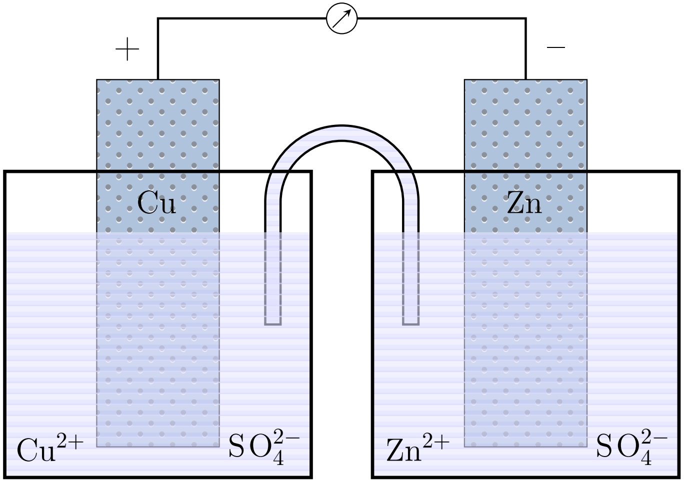
- Nernst equation for hydrogen electrode $2H^+ + 2e \rightleftarrows H_2$:
$$E = 0.000 + \frac{0.05916}{2}\lg\frac{a^2(H^+)}{p(H_2)/p_0} = -0.05916pH$$

- Nernst equation for metal electrode $M^{n+} + ne \rightleftarrows M$:
$$E = E^\circ(M^{n+}/M) + \frac{0.05916}{n}\lg a(M^{n+})$$

3 Galvanic element (cell)

A definition of galvanic cell

- A galvanic cell consist of two electrodes connected together by external circuit, for example **Daniel-Jacobi element**



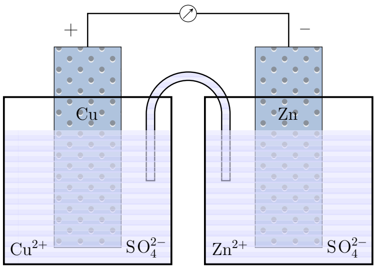
Equilibria establishing on electrodes:
$Zn^{2+} + 2e \rightleftarrows Zn$, $E^\circ = -0.76$ V

$Cu^{2+} + 2e \rightleftarrows Cu$, $E^\circ = +0.34$ V

- Galvanic cell scheme
  - The electrode which has a higher potential is *a cathode*
  - The electrode which has a lower potential is *an anode*
  - $\underbrace{Zn|Zn^{2+}}_{\text{anode}} || \underbrace{Cu^{2+}|Cu}_{\text{cathode}}$

Processes in galvanic element

- Charged particles begin to move when the external circuit is closed



  - The *electrons* are moving from anode to cathode *in external circuit.*
  - The *cations* are moving from anode to cathode *in solution.*
  - C: $Cu^{2+} + 2e = Cu$ – reduction
    A: $Zn - 2e = Zn^{2+}$ – oxidation

- Reaction equation summary:
$Cu^{2+} + Zn = Cu + Zn^{2+}$ or $CuSO_4 + Zn = Cu + ZnSO_4$

- The most important quantity is *electromotive force (EMF)*:

  - ${}_{\Delta}E = E_{\mathrm{c}} - E_{\mathrm{a}}$
  - ${}_{\Delta}G = -nF{}_{\Delta}E$

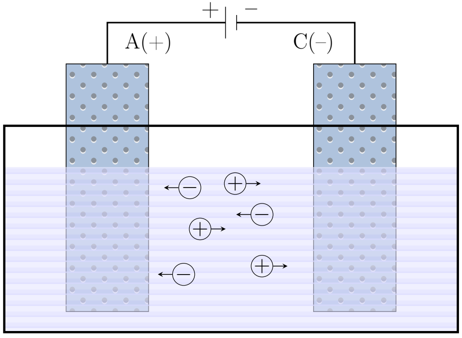
- The polarization is the EMF (${}_{\Delta}E$) change in nonequilibrium conditions (when the reaction occurs)

4 Electrolysis

4.1 Definitions

- Electrolysis is a process that occurs in the electrochemical system when the direct current (from external source) passes through it

- The charged particles are moving because of the closed circuit



*A*nions are moving to *a*node
*C*ations are moving to *c*athode
C: $\mathrm{Na}^+ + e = \mathrm{Na}$ – reduction
A: $2\mathrm{Cl}^- - 2e = \mathrm{Cl}_2$ – oxidizing
Summary: $2\mathrm{NaCl} \xrightarrow{\text{els}} 2\mathrm{Na} + \mathrm{Cl}_2$

$$\boxed{U =_{\Delta} E +_{\Delta} E_{\text{polariz}} + I(r_1 + r_2)}$$

- Despite the electrodes being charged here in opposite to how they are charged in the galvanic element, the function of each electrode remains the same:
  - *C*athode (+ in galvanic cell, − in the electrolyzer) is the place at where the *R*eduction occurs (both letters are consonants)
  - *A*node (− in galvanic cell, + in the electrolyzer) is the place at where the *O*xidation occurs (both letters are vowels)

4.2 Faraday laws

Faraday laws of electrolysis

- Two *Faraday laws of electrolysis* are quantitative relationships based on the electrochemical research published by Michael Faraday in 1833:
  1. the amount of chemical change produced by current at an electrode-electrolyte boundary is proportional to the quantity of electricity used, and
  2. the amounts of chemical changes produced by the same quantity of electricity in different substances are proportional to their equivalent weights

- The united Faraday laws expression:

- $$m(\mathrm{A}) = \frac{M(\mathrm{A}) \cdot I \cdot t}{nF} \cdot \text{C.E., or } V = \frac{V_m \cdot I \cdot t}{nF} \cdot \text{C.E., where:}$$
  - M is a molar mass, g/mol;
  - I is current, A;
  - t is time, s;
  - F is Faraday constant, Coul/mol;
  - n is number of electrons;
  - C.E. is current efficiency, $0 < \text{C.E.} \leq 1$

4.3 Cathodic processes

- Electrolysis of solutions: concurrent ions appeared, H^+ and OH^- ($H_2O \rightleftarrows H^+ + OH^-$)
- *Process which has a highest potential occurs as a cathodic one*
- All the metals can be separated into three groups
  - Metals which has $E^\circ < -1.66$ V (leftmost of Al)
  - Metals which has $E^\circ > 0$ V (rightmost of H)
  - Metals which has $-1.66 \text{ V} < E^\circ < 0$ V
- Cathodic processes:

$E^\circ < -1.66$ V	$2H_2O + 2e = H_2 + 2OH^-$ (pH $\geqslant 7$) or $2H^+ + 2e = H_2$ (pH < 7)
$-1.66 \text{ V} < E^\circ < 0$ V	$2H_2O + 2e = H_2 + 2OH^-$ $M^{n+} + ne = M$ ($Co^{2+} + 2e = Co$)
$E^\circ > 0$ V	$M^{n+} + ne = M$ ($Ag^+ + e = Ag$)

4.4 Anodic processes

- *Process which has a lowest potential occurs as an anodic one*
- Concurrent anodic processes:
  - Oxidation of anodic material
    $M - ne = M^{n+}$
    Inert anodic materials (Pt, graphite) don't react!

- Oxidation of electrolyte anions
  $2\mathrm{Hal}^- - 2e = \mathrm{Hal}_2$ (Hal = Cl, Br, I)
  $2\mathrm{S}^{2-} - 2e = \mathrm{S}$
- Oxidation of solvent
  - pH $\leqslant$ 7: $2\mathrm{H_2O} - 4e = \mathrm{O_2} + 4\mathrm{H}^+$
  - pH $>$ 7: $4\mathrm{OH}^- - 4e = \mathrm{O_2} + 2\mathrm{H_2O}$

4.5 Examples

- Electrolysis scheme for $\mathrm{CuCl_2}$ solution
  - C: $\mathrm{Cu}^{2+} + 2e = \mathrm{Cu}$
  - A: $2\mathrm{Cl}^- - 2e = \mathrm{Cl_2}$
  - Summary: $\mathrm{CuCl_2} = \mathrm{Cu} + \mathrm{Cl_2}$
- Electrolysis scheme for $\mathrm{Sn(NO_3)_2}$ solution
  - C: $\mathrm{Sn}^{2+} + 2e = \mathrm{Sn}$
    $2\mathrm{H_2O} + 2e = \mathrm{H_2} + 2\mathrm{OH}^-$
  - A: $2\mathrm{H_2O} - 4e = \mathrm{O_2} + 4\mathrm{H}^+$ (or $\mathrm{Sn} - 2e = \mathrm{Sn}$)
  - $\mathrm{Sn}^{2+} + 2\mathrm{H_2O} + 2\mathrm{H_2O} = \mathrm{Sn} + \mathrm{H_2} + 2\mathrm{OH}^- + \mathrm{O_2} + 4\mathrm{H}^+$
    cancelling: $\mathrm{Sn}^{2+} + 2\mathrm{H_2O} = \mathrm{Sn} + \mathrm{H_2} + \mathrm{O_2} + 2\mathrm{H}^+$.
    Summary: $\mathrm{Sn(NO_3)_2} + 2\mathrm{H_2O} = \mathrm{Sn} + \mathrm{H_2} + \mathrm{O_2} + 2\mathrm{HNO_3}$
- Electrolysis scheme for NaOH solution
  - C: $2\mathrm{H_2O} + 2e = \mathrm{H_2} + 2\mathrm{OH}^-$
  - A: $4\mathrm{OH}^- - 4e = \mathrm{O_2} + 2\mathrm{H_2O}$
  - Summary: $2\mathrm{H_2O} = 2\mathrm{H_2} + \mathrm{O_2}$