

General and Inorganic Chemistry Department,  
National Technical University “Kharkiv Polytechnic Institute”

**ELECTROCHEMICAL PROCESSES**



Responsible Lecturer:  
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## 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



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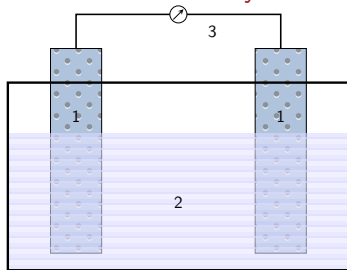
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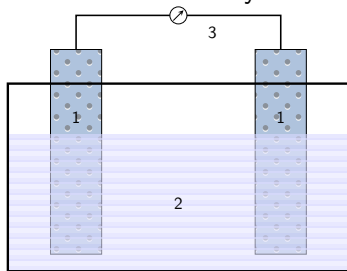
Solution (or melt) is the conductor of the **second kind**.

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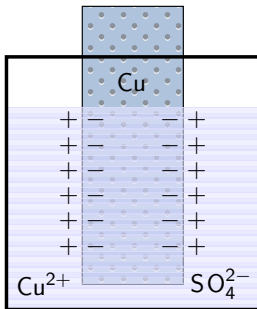
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## STANDARD ELECTRODE POTENTIAL

- There is double electrical layer on the electrode surface

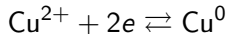


Copper plate in  $\text{CuSO}_4$  solution:

the Cu **atoms** are on the plate;

the  $\text{Cu}^{2+}$  **ions** are in the solution.

An equilibrium establishes on the interface:



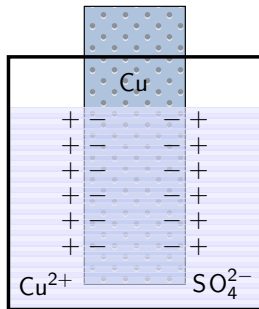
The **electrode potential**  $E$  establishes on the electrode due to this equilibrium.

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



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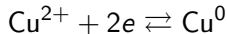


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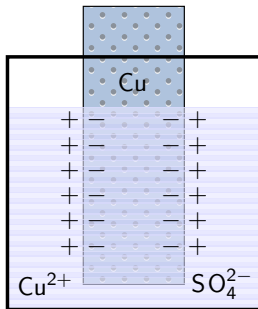
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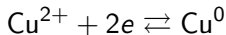


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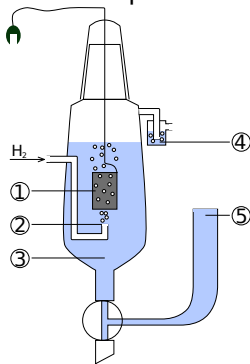
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## STANDARD HYDROGEN ELECTRODE

- The standard potential of  $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$  system is taken equal to 0.000 Volts exactly



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

- Platinized platinum electrode,
- Hydrogen gas bubbles,
- Acid solution with  $a(\text{H}^+) = 1 \text{ mol/L}$ ,
- Hydroseal for prevention of oxygen interference,
- 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  $\text{M}^{n+} + ne \rightleftharpoons \text{M}$  it defines the so-called metal activity series: for example:

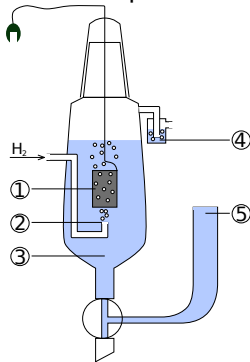
$E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ , so zinc is more active than hydrogen,

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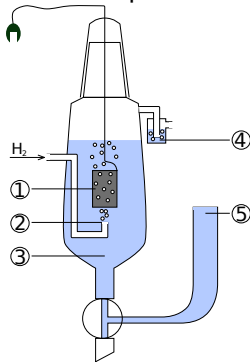
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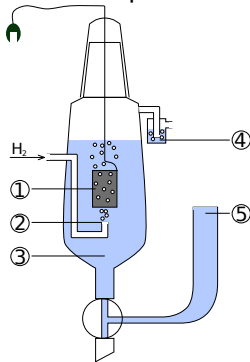
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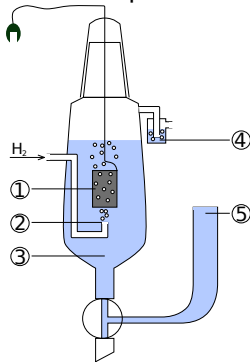
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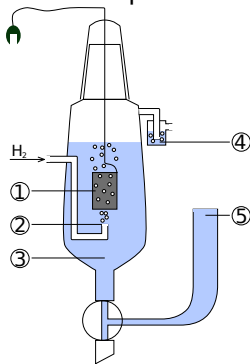
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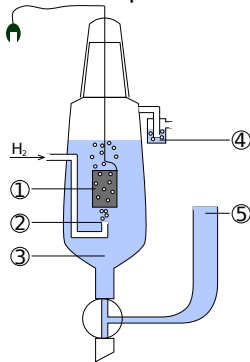
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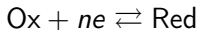
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- **Nernst equation** determines a potential ( $E$ ) of the system:



depending on conditions ( $T$ ,  $c$ )

$$E(\text{Ox}/\text{Red}) = E^\circ(\text{Ox}/\text{Red}) - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]}, \text{ where:}$$

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  - $F = eN_A = 96485$  Coul/mol is Faraday constant;
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- Nernst equation form at  $T = 298$  K:

$$E = E^\circ + \ln 10 \cdot \frac{RT}{nF} \lg \frac{[\text{Ox}]}{[\text{Red}]} = E^\circ + \frac{0.05916}{n} \lg \frac{[\text{Ox}]}{[\text{Red}]}$$

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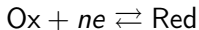
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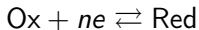
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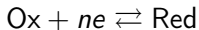
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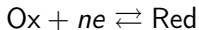
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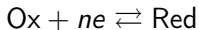
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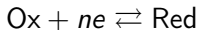
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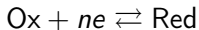
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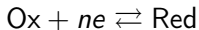
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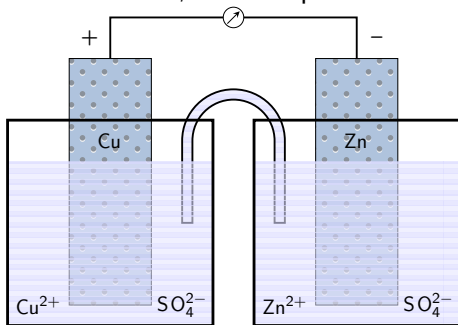
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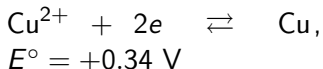
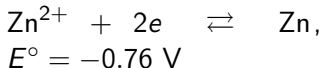


## A DEFINITION OF GALVANIC CELL

- A galvanic cell consist of two electrodes connected together by external circuit, for example DANIEL-JACOBI ELEMENT



Equilibria establishing on electrodes:



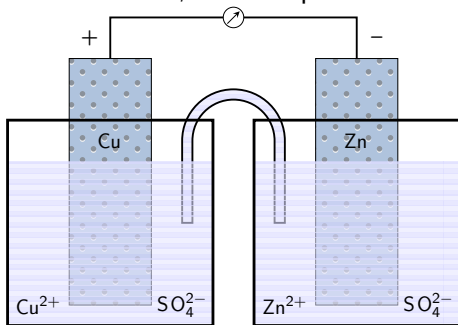
- Galvanic cell scheme

- The electrode which has a higher potential is a cathode
- The electrode which has a lower potential is an anode

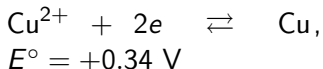
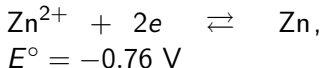


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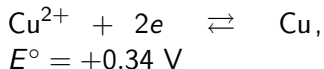
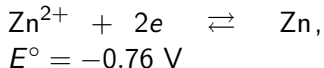


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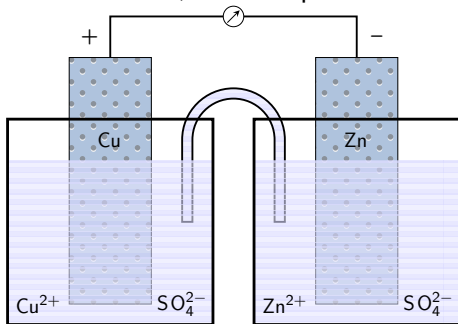
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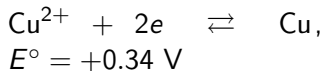
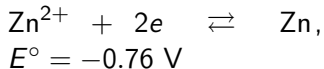


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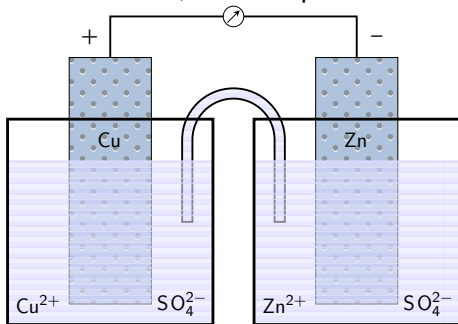
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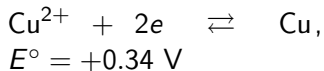
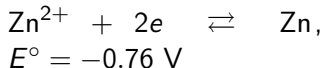


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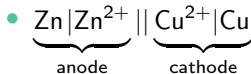


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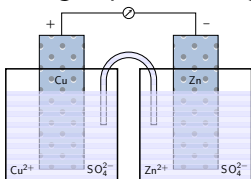
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# PROCESSES IN GALVANIC ELEMENT

- 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:  $\text{Cu}^{2+} + 2e = \text{Cu}$  – reduction
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- Reaction equation summary:



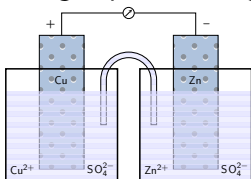
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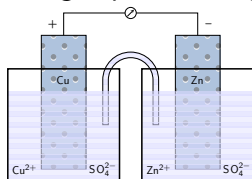
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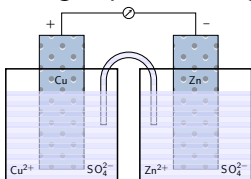


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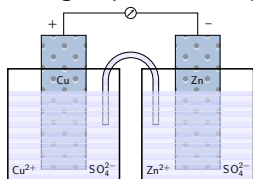
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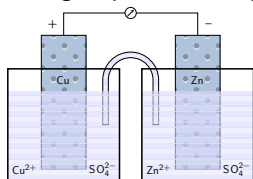
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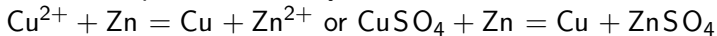
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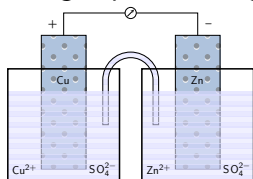
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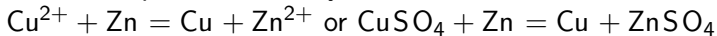
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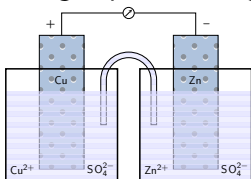
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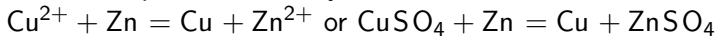
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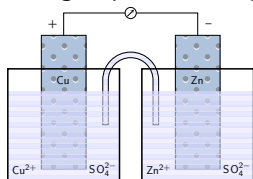
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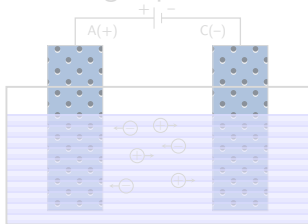


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## ELECTROLYSIS: DEFINITIONS

- 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



Anions are moving to anode

Cations are moving to cathode

C:  $\text{Na}^+ + e = \text{Na}$  – reduction

A:  $2\text{Cl}^- - 2e = \text{Cl}_2$  – oxidizing

Summary:  $2\text{NaCl} \xrightarrow{\text{els}} 2\text{Na} + \text{Cl}_2$

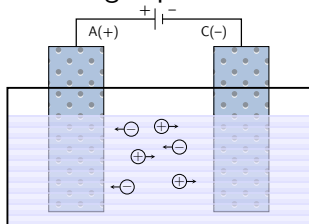
$$U = \Delta E + \Delta E_{\text{polariz}} + I(r_1 + r_2)$$

- 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:



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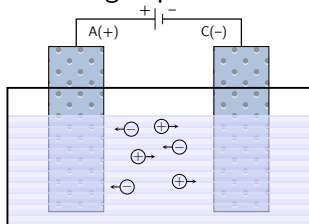
\* Cathode (+ in galvanic cell, – in the electrolyzer) is the place at where the Reduction occurs (both letters are consonants)

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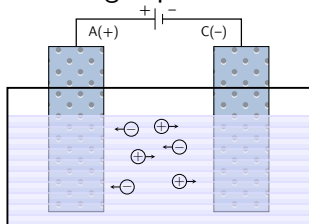
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Cations are moving to **c**athode

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Summary:  $2\text{NaCl} \xrightarrow{\text{els}} 2\text{Na} + \text{Cl}_2$

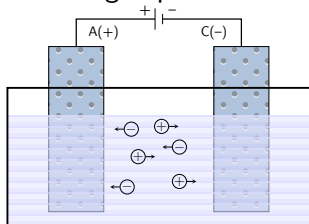
$$U = \Delta E + \Delta E_{\text{polariz}} + I(r_1 + r_2)$$

- 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)
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## ELECTROLYSIS: 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



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## 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:

$$m(A) = \frac{M(A) \cdot I \cdot t}{nF} \cdot \text{C.E.}, \text{ or } V = \frac{V_m \cdot I \cdot t}{nF} \cdot \text{C.E.}, \text{ where:}$$



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- Electrolysis of solutions: concurrent ions appeared,  $H^+$  and  $OH^-$   
( $H_2O \rightleftharpoons H^+ + OH^-$ )
- Process which has a highest potential occurs as a cathodic one
- All the metals can be separated into three groups
  - Metals which has  $E^0 < -1.10 V$  (leftmost of  $H_2$ )
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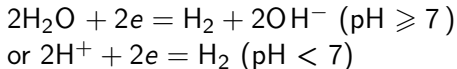
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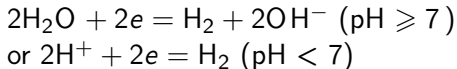
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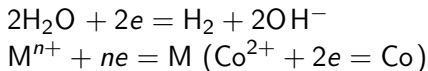
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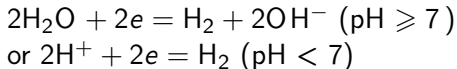
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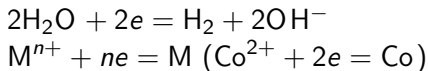
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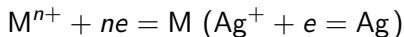
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- Process which has a lowest potential occurs as an anodic one
- Concurrent anodic processes:
  - Oxidation of anodic material  
 $M - ne = M^{n+}$   
Inert anodic materials (Pt, graphite) don't react!
  - Oxidation of electrolyte anions  
 $2\text{Hal}^- - 2e = \text{Hal}_2$  (Hal = Cl, Br, I)  
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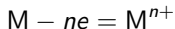
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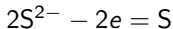
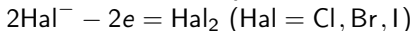
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## ELECTROLYSIS: EXAMPLES

- Electrolysis scheme for  $\text{CuCl}_2$  solution
  - C:  $\text{Cu}^{2+} + 2e = \text{Cu}$
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  - Summary:  $\text{CuCl}_2 = \text{Cu} + \text{Cl}_2$
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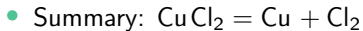
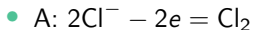
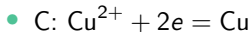


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