«Electrochemical processes»

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*Lecture plan

1. Basic concepts

2. Galvanic Cells

3. Electrolysis

4. Corrosion

1. Basic concepts

***<u>Electrochemical processes</u>** are processes of mutual transformation of chemical and electrical forms of energy.

1 group

the process of converting chemical energy into electrical energy
$\Delta G<0$

2 group

- the process of converting electrical energy into chemical energy
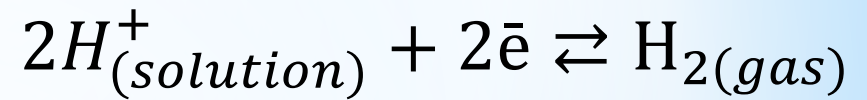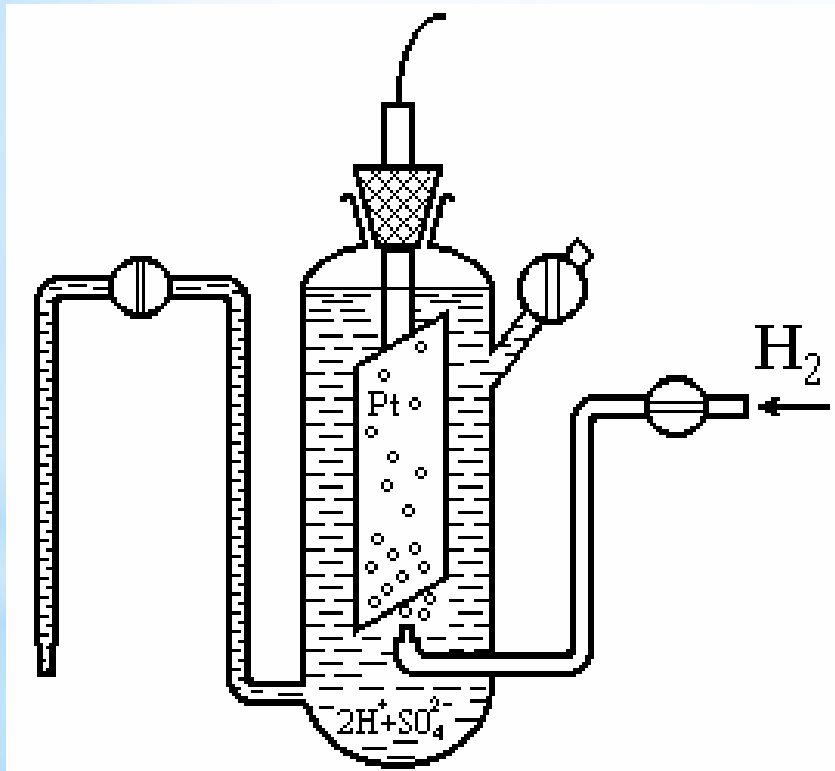- $\Delta G>0$

1. Basic concepts

The electrode potential is the potential difference that occurs at the metal-solution interface if a metal plate is immersed in water or a solution containing metal ions.

$$Me + mH_2O \rightleftarrows Me^{n+}(H_2O)_m + ne$$

1. Basic concepts

Standard hydrogen electrode

$$2H^+_{(solution)} + 2\bar{e} \rightleftarrows H_{2(gas)}$$

$$\varphi^0_{2H^+/H_2} = 0 \text{ B}$$

1. Basic concepts

The standard electrode potential is the electrode potential measured under standard conditions (**T = 298 К; [Me^{n+}] = 1 mol/l, P = 101.3 kPa**) relative to a standard hydrogen electrode.

1. Basic concepts

Element	Half-cell reaction	Voltage, E*
Potassium	$K^+ + e \rightarrow K$	-2.93
Calcium	$Ca^{2+} + 2e \rightarrow Ca$	-2.87
Sodium	$Na^+ + e \rightarrow Na$	-2.71
Magnesium	$Mg^{2+} + 2e \rightarrow Mg$	-2.37
Aluminum	$Al^{3+} + 3e \rightarrow Al$	-1.66
Zinc	$Zn^{2+} + 2e \rightarrow Zn$	-0.76
Iron	$Fe^{2+} + 2e \rightarrow Fe$	-0.44
Nickel	$Ni^{2+} + 2e \rightarrow Ni$	-0.25
Tin	$Sn^{2+} + 2e \rightarrow Sn$	-0.14
Lead	$Pb^{2+} + 2e \rightarrow Pb$	-0.13
Hydrogen	$2H^+ + 2e \rightarrow H_2$	-0.00
Copper	$Cu^{2+} + 2e \rightarrow Cu$	0.34
Mercury	$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.79
Silver	$Ag^+ + e \rightarrow Ag$	0.80
Gold	$Au^{3+} + 3e \rightarrow Au$	1.50

	$E°$ in volt
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	+1.77
$Au^-(aq) + e^- \rightarrow Au(s)$	+1.68
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(1)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
$Ag^-(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightarrow H_2S(g)$	+0.14
$2H^-(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.23
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.28
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.03
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.67
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	−2.34
$Na^+(aq) + e^- \rightarrow Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	−2.87
$K^-(aq) + e^- \rightarrow K(s)$	−2.93
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.02

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1. Basic concepts

Nernst formula

$$\varphi_{Me^{n+}/Me} = \varphi^0 + \frac{RT}{nF}\ln[Me^{n+}],$$

where φ^0 – standard electrode potential of a metal,
n – the number of electrons involved in the process,
F – Faraday constant (96500 C/mol).

1. Basic concepts

Nernst formula by T=298 К

$$\varphi_{Me^{n+}/Me} = \varphi^0 + \frac{0,059}{n} \lg [Me^{n+}]$$

Nernst formula by standard conditions

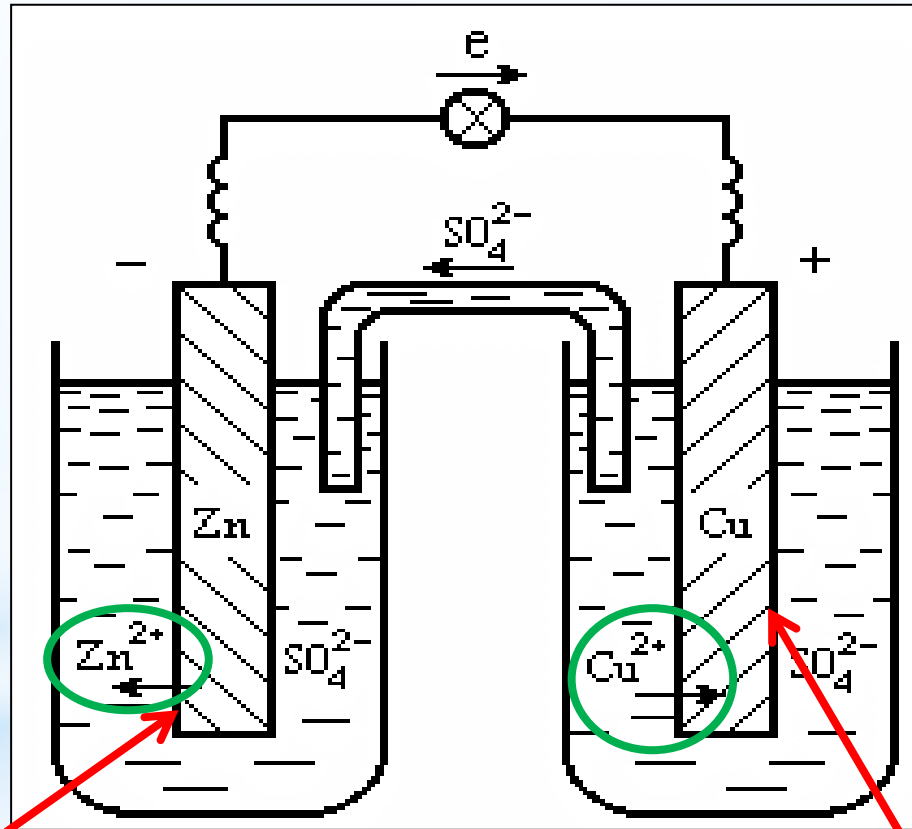$$\varphi_{Me^{n+}/Me} = \varphi^0$$

2. Galvanic Cells

A galvanic cell is a device that converts the energy of a chemical reaction into electrical energy due to the spontaneous occurrence of redox reactions on the electrodes.

Anode is an electrode made of more active with a lower φ^o.

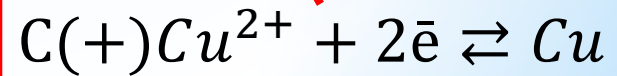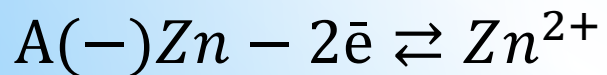**Cathode** is an electrode made of less active Me, with a large φ^o.

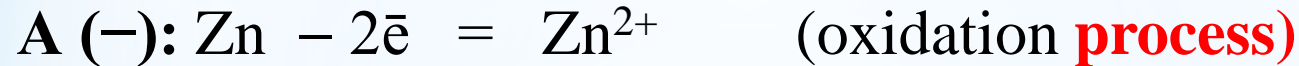# 2. Galvanic Cells

Galvanic cell by **Daniel and Jacobi**

$\varphi^0 = -0,76$ V

$\varphi^0 = +0,34$ V

$A(-)Zn - 2\bar{e} \rightleftarrows Zn^{2+}$

$C(+)Cu^{2+} + 2\bar{e} \rightleftarrows Cu$

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2. Galvanic Cells

Electrochemical scheme:

$$\textbf{A (-) Zn | ZnSO}_4 \textbf{ || CuSO}_4 \textbf{ | Cu (+) C}$$

A (−): $Zn - 2\bar{e} = Zn^{2+}$ (oxidation **process)**

+

C (+): $Cu^{2+} + 2\bar{e} = Cu^0$ (**recovery** process**)**

———————————

$$\textbf{Zn + Cu}^{2+} = \textbf{Zn}^{2+} + \textbf{Cu}$$ (ionic equation)

$$\textbf{Zn + CuSO}_4 = \textbf{ZnSO}_4 + \textbf{Cu}$$ (molecular equation)
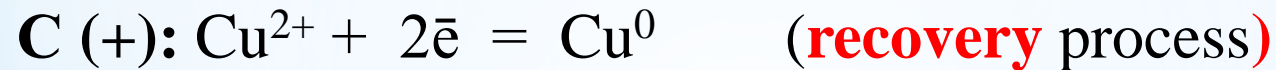
The current-forming reaction is the total reaction that takes place in a galvanic cell.

2. Galvanic Cells

   Electromotive force ГЭ (EMF) is the maximum difference in electrodes of this galvanic element, which is determined in equilibrium conditions.

EMF (The electrical power) $= \Delta\varphi = \varphi_{cathode} - \varphi_{anode}$

3. Electrolysis

Electrolysis is a sum of processes that occur on electrodes when an electric current is passed through an electrolyte solution or melt.

There are

■ electrolysis of **melts** and **solutions** and melts,
■ electrolysis with **inert** and **active** electrodes.

3. Electrolysis

At the **cathode** (-) the **recovery process** takes place,

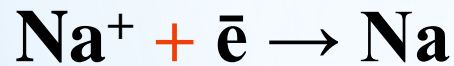and at the **anode** (+) the **oxidation process** takes place.
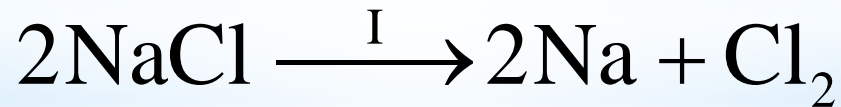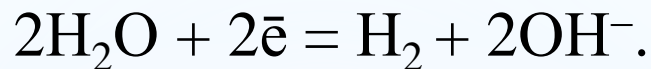
3. Electrolysis

Electrolysis of molten salt NaCl

$$NaCl \rightleftarrows Na^+ + Cl^-$$

Cathod(-):

$$Na^+ + \bar{e} \rightarrow Na$$

Anod(+):

$$2Cl^- - 2\bar{e} \rightarrow Cl_2$$

$$2NaCl \xrightarrow{I} 2Na + Cl_2$$

Overall reaction

3. Electrolysis

$$2H_2O + 2\bar{e} = H_2 + 2OH^-.$$

$$\varphi_{H^+/H_2} = \varphi^0 + \frac{0,059}{n}\lg\ [H^+] = 0 + \frac{0,059}{1}\lg[\ 10^{-7}] = -0,41V$$

Li K Ba Sr Ca Na Mg Al Mn Zn Cr Fe Cd Co Ni Sn Pb (H$_2$) Cu Hg Ag Pt Au

активные   средней   малоактивные
                  активности

$\varphi <<$ -0,41 V $\varphi \approx$ -0,41 V $\varphi >$ -0,41 V

3. Electrolysis

Cathodic processes

Li … Al	Mn … Cd	Co … Au
Water recovery	**Recovery Me and water recovery**	**Recovery Me**
$2H_2O+2e=H_2+2OH^-$	$Me^{n+}+ne = Me$ $2H_2O+2e=H_2+2OH^-$	$Me^{n+}+ne = Me$

3. Electrolysis

Anode processes

Simple anions Cl^-, Br^-, I^-, S^{2-} (**except F⁻**)	Complex anions (SO_4^{2-}, NO_3^- e.t.c.) and **F⁻**
Ion oxidation $2Cl^- - 2\bar{e} = Cl_2$	**Water oxidation** $2H_2O - 4\bar{e} = O_2 + 4H^+$

3. Electrolysis

$$AgNO_3 \leftrightarrow Ag^+ + NO_3^-$$

Cathode (-)   **Anod (+)**

$$Ag^+ + e = Ag$$ $$2H_2O - 4\bar{e} = O_2 + 4H^+$$

Overall reaction:

$$4AgNO_3 + 2H_2O \xrightarrow{I} 4Ag + O_2 + 4HNO_3$$
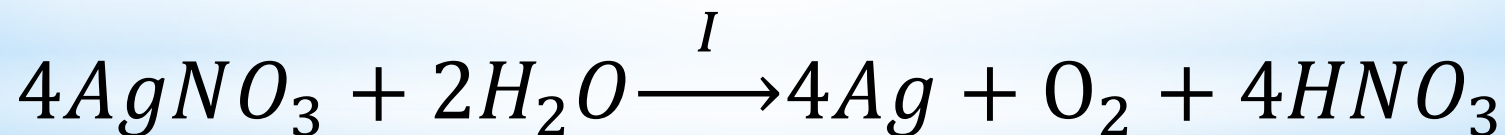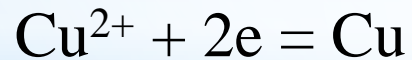
3. Electrolysis

Soluble (active) anode electrolysis

In solution $CuSO_4$ with anode - Cu :

Cathode (-)   **Anode (+)**

$Cu^{2+} + 2e = Cu$ $Cu - 2\bar{e} = Cu^{2+}$

3. Electrolysis

Quantitative Laws of Electrolysis - Faraday's Laws

<u>**I Law:**</u> «The mass of the electrolyte that has undergone transformation during electrolysis, as well as the mass of substances formed on the electrodes, is directly proportional to the amount of electricity passed through the electrolyte solution or melt»

$$m = k \cdot Q, \text{ где } Q = I \cdot \tau$$

m is a mass of substances (g),

Q is an amount of electricity (C),

I is current strength (A),

τ is electrolysis time (second).

3. Electrolysis

$$k = \frac{M_{эк}}{F}$$

$\dfrac{M_{эк}}{F}$ is an electrochemical equivalent,

$M_{эк}$ is an equivalent mass of a substance(g/mol),
F is a Faraday constant(96500 C /mol).

$$m = \frac{M_{эк} I \cdot t}{F} \eta$$

3. Electrolysis

$$V = \frac{V_{эк} I \cdot t}{F} \eta$$

V is a volume of released gas, *l*.

$V_{эк}$ is equivalent volume of gas, l/mol.

3. Electrolysis

II Law: «When the same electricity passes through a solution or melt of an electrolyte, the masses (volumes) of substances released on the electrodes are directly proportional to their electrochemical equivalents»

$$m = \frac{M_{эк}}{F}(when\ Q = const)$$

F is the amount of electricity required to release or convert one mole equivalent of a substance

4. Corrosion

Corrosion is a spontaneous process of destruction of metals as a result of their chemical or electrochemical interaction with the environment.

4. Corrosion

Chemical corrosion is corrosion characteristic of non-conductive media. There is a direct heterogeneous interaction of the metal with the environmental oxidizer.

Gas corrosion;

Corrosion in non-electrolytes (aggressive organic liquids - sour oil)

4. Corrosion

Electrochemical corrosion is the destruction of metal in an electrolyte environment with the appearance of an electric current inside the system**.**

4. Corrosion

Mechanism

1. The cause of corrosion of metals in water is the thermodynamic instability of most metals when they come into contact with the environment.

2. In order for the ion-atoms to leave the surface of the metal, there must be a break in the bond between the ion-atom and the electron.

3. The source of energy necessary to break the bond is the process of hydration, accompanied by the release of energy.

4. Corrosion

The cause of electrochemical corrosion is the formation of microgalvanic pairs on the metal surface.

due to :
- ✓ presence of impurities,
- ✓ inhomogeneity of the Me surface,
- ✓ uneven distribution of strains in Me,
- ✓ inhomogeneity of the liquid phase,
- ✓ difference in external conditions (P, T)

4. Corrosion

Depending **on environment** :

❑ In electrolyte solutions (acids, bases, salts, natural water).

❑ Atmospheric corrosion - in the environment of any moist gas.

❑ Soil corrosion.

❑ Marine corrosion - (dissolved salts, gases and organic matter).

❑ Biocorrosion - (vital activity of organisms that produce gases such as CO_2, H_2S).

❑ Electrocorrosion - occurs under the action of stray currents on underground structures, as a result of the work of electric railways, tram lines.

4. Corrosion

Electrochemical polarization is the process of deviation of the potential from the equilibrium one under the action of an external potential (or during the flow of current).

Anode polarization

The reasons:

- Metal ions go into solution more slowly than electrons are removed to the cathode part.
- Insufficient removal rate of metal ions that have passed into solution.
- The occurrence of anodic passivity due to the formation of passive films on the metal surface.

4. Corrosion

Cathodic polarization

The reason:

the low speed of the electrochemical reaction of the connection of depolarizers with electrons.

Corrosion of metals, in which the cathodic reaction is carried out with the release of hydrogen, is called corrosion of metals with **hydrogen depolarization.**

Conditions: in acid solutions, for example, acid dissolution of iron, zinc and other metals.

1. Corrosion

During electrochemical corrosion, two processes simultaneously occur on the metal surface:

anodic - metal oxidation : $\qquad$ $Me - n\bar{e} = Me^{n+}$

cathodic - reduction.

1. Corrosion

Hydrogen depolarization :

acidic medium (*φ=0 V*):

$$2H^+ + 2e = H_2$$

neutral (*φ = − 0,41 V*):

$$2H_2O + 2e = H_2 + 2OH^-$$

$$\varphi_{H^+/H_2} = \varphi^0 + \frac{0,059}{n}\lg\ [H^+] = 0 + \frac{0,059}{1}\lg[10^{-7}] = -0,41V$$

alkaline (*φ = − 0,83 V*):

$$\varphi_{H^+/H_2} = \varphi^0 + \frac{0,059}{n}\lg[H^+] = 0 + \frac{0,059}{1}\lg[10^{-14}] = -0,83\ V$$

$$\boldsymbol{\varphi_{H^+/H_2} = 0,059\lg[H^+] = -0,059pH}$$

1. Corrosion

Oxygen depolarization :

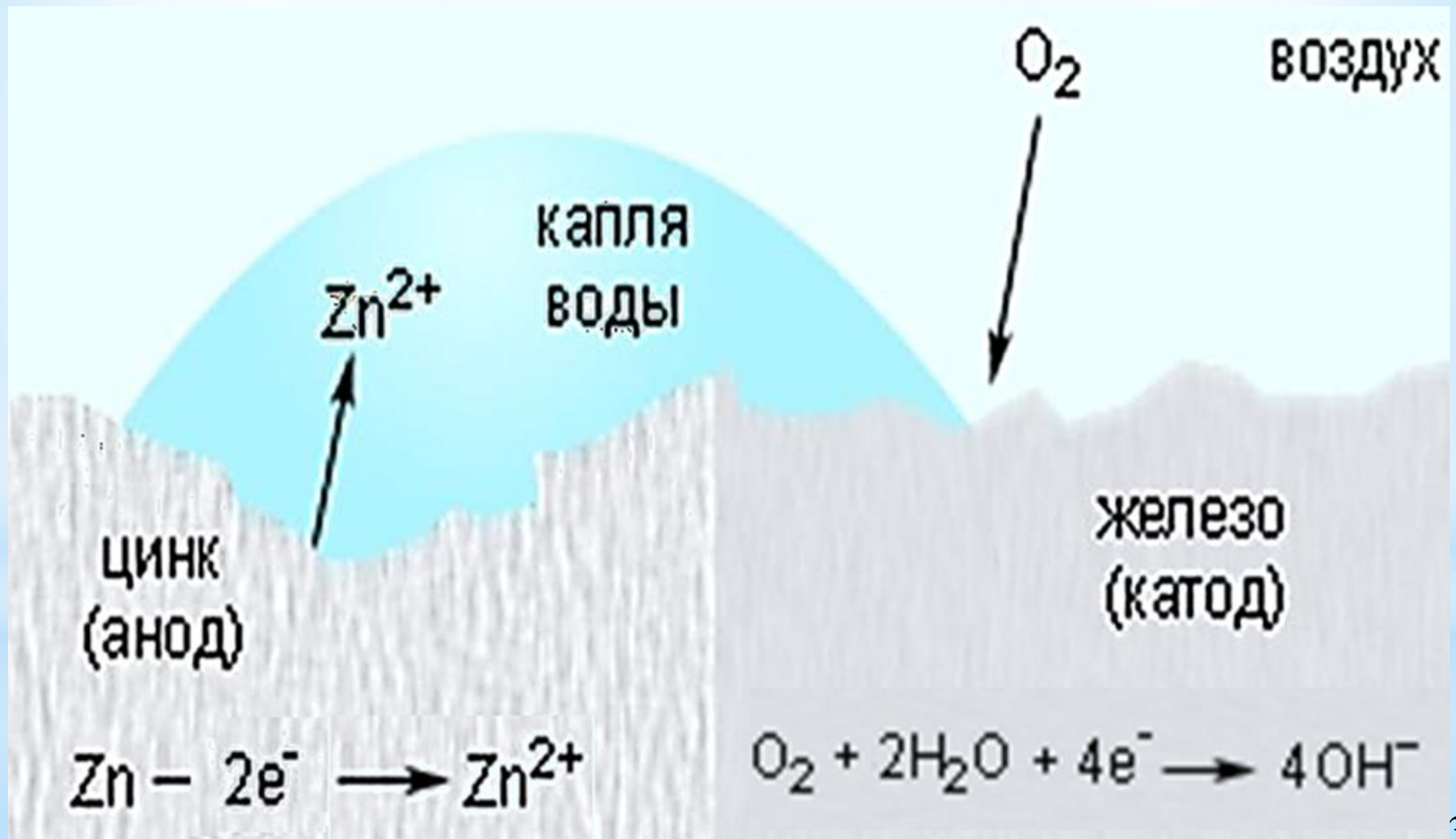**neutral** *($\varphi = 0,815$ V) and* **alkaline** medium *($\varphi = 0,4$ V)*:

$$O_2 + 2H_2O + 4\bar{e} = 4OH^-$$

acidic medium *($\varphi = 1,23$ V)*:

$$O_2 + 4H^+ + 4\bar{e} = 2H_2O$$
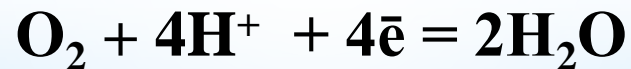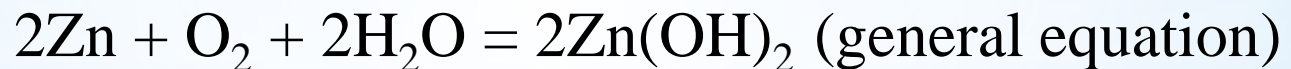
$$\boldsymbol{\varphi_{O_2/OH^-} = 1,23 - 0,059pH}$$

4. Corrosion

Contact corrosion

2. Corrosion

Diagram of a corrosion element :

A (−): $Zn - 2\bar{e} = Zn^{2+}$ (**oxidation** process)

C (+): $O_2 + 2H_2O + 4\bar{e} = 4OH^-$ (**recovery** process)

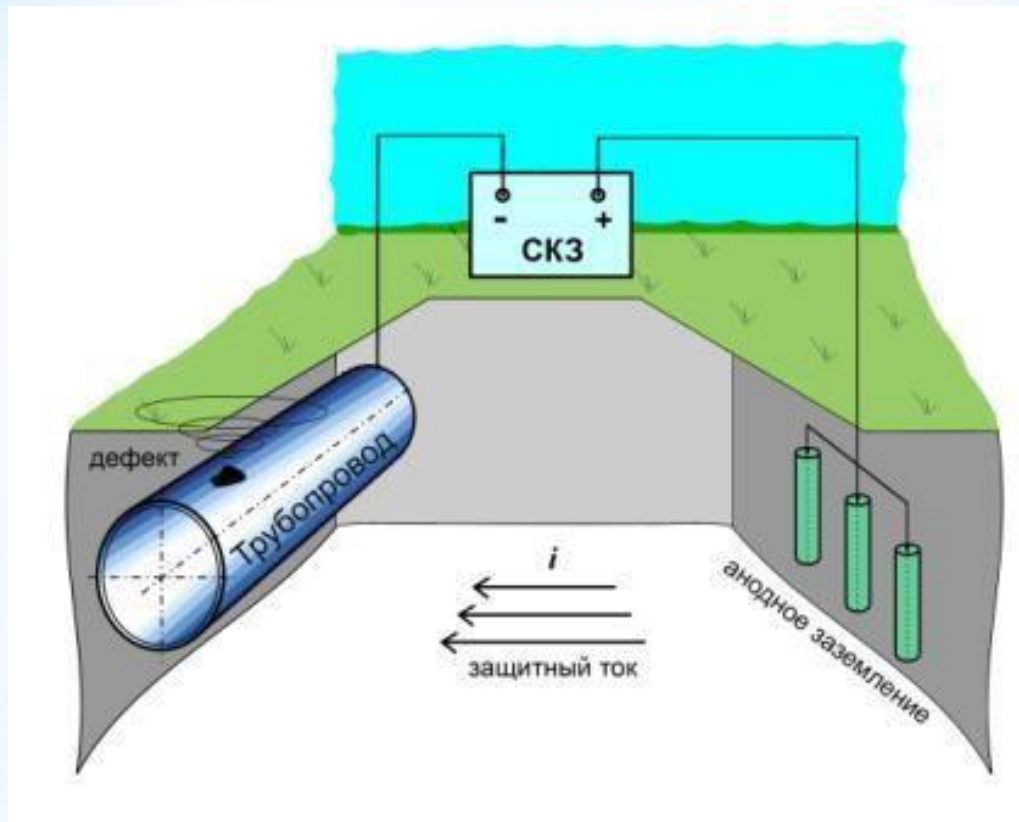$2Zn + O_2 + 2H_2O = 2Zn(OH)_2$ (general equation)
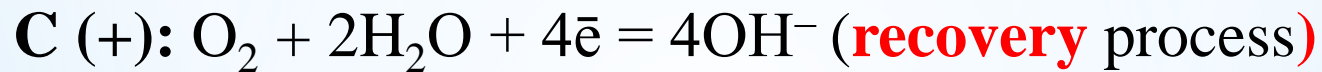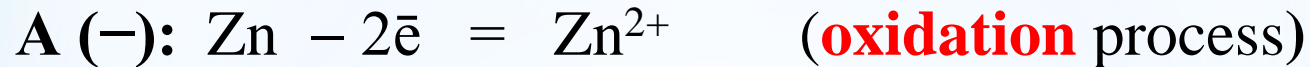
Anode (-) Zn | Zn^{2+} || O_2, $2H_2O$, $4OH^-$ | Fe (+) Cathode

Protector method: a piece of a more active metal (protector) is attached to the protected metal structure, which serves as an anode and is destroyed in the presence of an electrolyte**.**

Cathodic protection consists in applying an external current to the product from the negative pole, which polarizes the cathodic areas of corrosive elements. The positive pole of the current source is connected to the anode. In this case, the corrosion of the protected structure is almost reduced to zero. The anode is gradually destroyed and must be replaced periodically.

1. task

The electromotive force (EMF) of the process that occurs when copper and cadmium come into contact in an acidic environment without access to oxygen (pH = 4) under standard conditions is _____V.

$$(\varphi^0_{Cd^{2+}/Cd^0} = -0,40V; \varphi^0_{Cu^{2+}/Cu^0} = +0,34V)$$

(*Write your answer to the nearest thousandth*)

The solution of the task

Anode (-) Cd | Cd^{2+} ‖ H^+, H_2 | Cu (+) Cathode

Cd is more active than Cu, therefore Cu is a Cathode, Cd is an anode.
A acidic medium (without O_2), therefore, the cathode is hydrogen depolarization.
To calculate the **EMF**, it is necessary to find electrode potentials:

$$\varphi_{anode} = \varphi^0 + \frac{RT}{nF}\ln[Cd^{2+}] = -0.40 + \frac{2.3 \cdot 8.314 \cdot 298}{2 \cdot 96500}\lg[1] = -0.40\,V$$

$$\varphi_{cathode} = \varphi_{H^+/H_2} = 0.059\lg[H^+] = -0.059\text{pH} = -0.059 \cdot 4 = -0.236\,V$$

$$EMF = \varphi_{cathode} - \varphi_{anode} = -0.236 - (-0.40) = 0.164\,V$$

Answer: EMF = 0,164 V

2. Task

Calculate the EMF of a galvanic cell composed of magnesium and lead electrodes, in which $[Mg^{2+}] = 0{,}1$ M; $[Pb^{2+}] = 0{,}001$ M.

The solution of the task

φ^0 (Mg^{2+}/Mg) = −2,37 V; φ^0 (Pb^{2+}/Pb) = −0,13 V;

φ^0 magnesium electrode is smaller, so Mg is a more active metal, and it will be an anode, and Pb is a cathode.

The following processes will proceed on the electrodes:

$$\text{Anode: } Mg - 2e = Mg^{2+},$$

$$\text{Cathode: } Pb^{2+} + 2e = Pb^0.$$
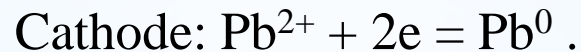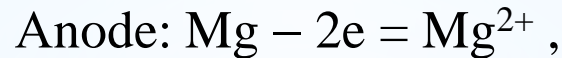
The diagram is recorded like this :   (Anode) **Mg│Mg^{2+}‖Pb^{2+}│Pb** (Cathode)

To calculate the EMF, it is necessary to find electrical potentials :

$$\varphi_{Mg^{2+}/Mg} = \varphi^0 + \frac{0,059}{n}\lg[Mg^{2+}] = -2,37 + 0,0295 \cdot \lg 0,1 = -2,4V$$

$$\varphi_{Pb^{2+}/Pb} = \varphi^0 + \frac{0,059}{n}\lg[Pb^{2+}] = -0,13 + 0,0295 \cdot \lg 0,001 = -0,22V$$

$$EMF = \varphi_{cathode} - \varphi_{anode} = -0,25 - (-2,4) = 2,15V$$