NATIONAL TECHNICAL UNIVERSITY
“KHARKIV POLYTECHNIC INSTITUTE”
MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE

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ELECTROCHEMICAL PROCESSES AND SYSTEMS: APPLICATION FOR TUTORS

Kharkiv 2018

УДК 54(075.8)
Е 43

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Друкується за рішенням вченої ради
Національного технічного університету “ХПІ”,
протокол № 9 від 30 листопада 2018 р.

Е 43 Electrochemical processes and systems: application for tutors : monography / edited by M. Ved’ / M. Ved’, M. Volobuyev, I. Stepanova, I. Yermolenko, A. Karakurkchi. – Kharkiv : NTU “KhPI”, 2018. – 112 c.

ISBN

Розглянуто особливості окисно-відновних реакцій і принципи їх балансування залежно від складу середовища. Викладено фундаментальні уявлення про електрохімічні процеси і системи. Проаналізовано перебіг реакцій і принципи функціонування хімічних джерел електричної енергії та систем електролізу. Узагальнено уявлення щодо хімічних властивостей металів, корозійної стійкості у середовищах різної агресивності та наведено принципи організації захисту від руйнування. Запропоновано багатоваріантні завдання та вправи для аудиторної та самостійної роботи студентів і аспірантів. Розраховано на викладачів, аспірантів і студентів вищих навчальних закладів спеціальностей "Хімічні технології та інженерія”, "Біотехнології та біоінженерія", "Нафтогазова інженерія та технології".

The features of redox reactions and the principles of their balancing according to the medium composition are considered. The basic representations about electrochemical processes and systems are outlined. The reactions and principles of chemical sources of electric energy and electrolysis systems functioning are analyzed. A general idea is given about the chemical properties of metals, corrosion resistance in environments of various aggressiveness, and the protection principles are given. Multivariate tasks and exercises for students, and PhD student’s classroom and independent work are offered. For teachers, PhD students and students of universities of specialties "Chemical technologies and engineering", "Biotechnologies and bioengineering", "Oil and gas engineering and technologies".

УДК 54(075.8)

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CHAPTER 1 OXIDATION-REDUCTION REACTIONS

1.1 BASIC CONCEPTS AND DEFINITIONS

Reactions that occur with changes in oxidation states of elements in molecules, ions or crystalline substances are called oxidation-reduction reaction or *redox* reactions.

Redox reactions are a family of reactions that are concerned with the transfer of electrons between species. Oxidation is the loss of electrons or an increase in oxidation state of element in a molecule, atom, or ion, and reduction is the gain of electrons or a decrease in oxidation state of a particle (Fig. 1.1).

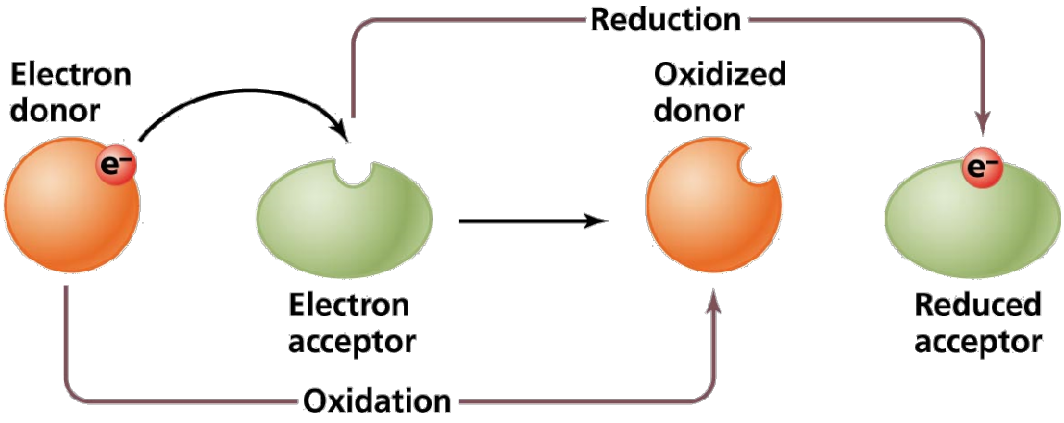


Figure 1.1. Scheme of a red-ox reaction

Redox reactions are a matched set: there can't be an oxidation reaction without a reduction reaction happening simultaneously. The oxidation alone and the reduction alone are each called a *half-reaction*, because two half-reactions always occur together to form a net reaction. In Red-Ox processes, the reductant transfers electrons to the oxidant. Thus, in the reaction, the *reductant* or *reducing agent* (electron donor)

loses electrons and is oxidized, and the *oxidant* or *oxidizing agent* (electron acceptor) gains electrons and is reduced.

The pair of an oxidizing and reducing agent that are involved in a particular reaction is called a red-ox pair.

The main rule of redox reaction is: the number of electrons which excess in the oxidation half reaction must be equal the number of electrons consumed by the reduction half reaction. The half-reaction must be balanced with respect to electric charge:

$H_2 + F_2 \rightarrow 2\,HF$

$H_2 \rightarrow 2H^+ + 2e$ reducing agent – oxidation

$F_2 + 2e \rightarrow 2F^-$ oxidizing agent – reduction

Redox reactions seem to be of following types:

- Combination – two reactants combine to form one product

$$2Mg + O_2 \rightarrow 2MgO;$$

- Decomposition – one reactant forms two or more products

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O;$$

- Displacement – a metal will displace a less reactive metal in a metal salt solution

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu;$$

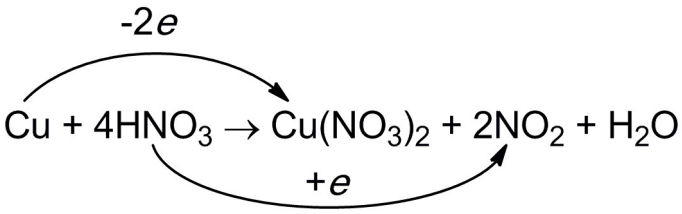
- Combustion (burning) occurs so rapidly that noticeable heat and light are produced:

coal $C + O_2 \rightarrow CO_2$;

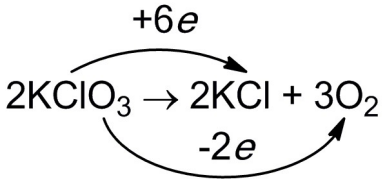
gasoline $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$.

Types of redox reactions at the location of the oxidizer and reducing agent:

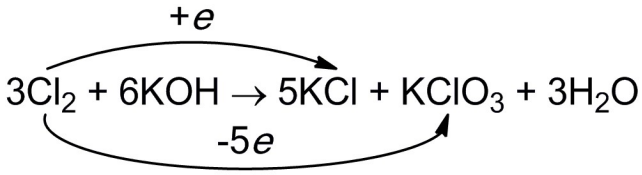
- intermolecular oxidation-reduction – an oxidizing agent and a reducing one are found in molecules of various substances:



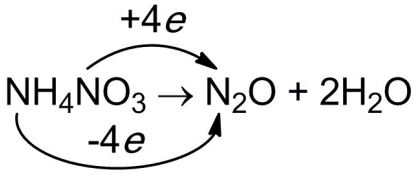
- Intramolecular oxidation-reduction – the oxidizing agent and the reducing one are in the same molecule:



- Disproportionation (self-oxidation-self-reduction) – the same element is both an oxidizing and a reducing agent:



- Reproportionation (proportionation) – from two different oxidation numbers of the same element, one degree of oxidation is obtained:



In the electronic balance method, the number of electrons lost and gained is calculated from the values of the oxidation number (ox#) of the elements before and after the reaction:

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$$

$$\left.\begin{array}{l} Cr^{+6} + 3e \rightarrow Cr^{+3} \\ 2N^{-3} - 6e \rightarrow N_2^0 \end{array}\right| 6 \left|\begin{array}{ll} 2 & \text{– oxidizing agent} \\ 1 & \text{– reducing agent} \end{array}\right.$$

Substances can show only reductive, only oxidative properties or redox duality. The main factors of the redox properties of substances are following: the nature of substances; oxidation number of the element in a compound; pH of a medium; concentration of reactants; temperature etc.

A good reducing agent must be able to donate electrons readily. Metals can be attributed to the number of strong reducing agents:

$$Zn + O_2 \rightarrow 2ZnO,$$

Zn – reductant (electron donor),

O_2 – oxidant (electron acceptor).

Among the elements, low electronegativity is characteristic of good reductant:

$$2F_2 + O_2 \rightarrow 2OF_2,$$

O_2 – reductant (EN=3.44),

F_2 – oxidant (EN=3.98).

Molecules and ions which contain relatively electropositive elements with low oxidation numbers are also good reductants:

$$S + O_2 \rightarrow SO_2,$$

S^0 – reductant (EN=2.58),

O_2 – oxidant (EN=3.44).

Oxidizing agents (oxidants) must be able to accept electrons readily. Highly electronegative elements can do this:

$$Cl_2 + Cu \rightarrow CuCl_2,$$

Cl_2 – oxidant (EN=3.16),

Cu – reductant (EN=1.90).

Molecules or ions which contain relatively electronegative elements and even some metals which have high ox# are oxidizing agents.

Common reducing agents are the metals due to the structure of their external electronic sublevels and low electronegativity (EN). Metals have low ionization energies and so they can lose electrons fairly easily. Some of them (alkali and alkaline-earth) can even reduce Hydrogen from water:

$$2Li(s) + 2H_2O(l) \rightarrow 2Li^+(aq) + 2OH^-(aq) + H_2(g).$$

Other metals (Fe, Zn) can reduce Hydronium ions:

$$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + 2H_2O(l) + H_2(g).$$

There are a few metals that will not dissolve in just any acid but instead require an acid like HNO_3 whose anion is a good oxidizing agent:

$$Hg(s) + 8\ H_3O^+(aq) + 2NO_3^-(aq) \rightarrow 3Hg^{2+}(aq) + NO(g) + 12H_2O.$$

Common oxidizing agents are nonmetals with high electronegativity and anions which include the element with the highest oxidation state: NO_3^-, IO_3^-, MnO_4^-, $Cr_2O_7^{2-}$.

All four elemental Halogens, F_2, Cl_2, Br_2 and I_2, are able to accept electrons according to the half-equation:

$$X_2 + 2e \rightarrow 2X^-, \quad X = F, Cl, Br, I.$$

The oxidizing power of the halogens decreases in the order $F_2 > Cl_2 > Br_2 > I_2$. Fluorine is such a strong oxidizing agent that it can react with water and oxidize Oxygen:

$$2F_2 + 6H_2O \rightarrow 4H_3O^+ + 4F^- + O_2.$$

O_2 is very slightly weaker than chlorine, but considerably stronger than bromine.

Substances which include the element with the highest state of oxidation exhibit only oxidation properties. The highest state of element oxidation equals, as rule, the number of the group in the periodic system (PS), in which it is located. Substances containing element with the lowest state of oxidation, show only reduction properties. If this element is metal, its lower oxidation state is zero; for nonmetals the lowest oxidation sate is calculated as (number of PS group – 8). Substances containing element with the intermediate oxidation state have both oxidation and reduction properties. Some examples of substances containing chlorine or manganese in various oxidation states and appropriative redox properties of the compounds are shown on Fig. 1.2.

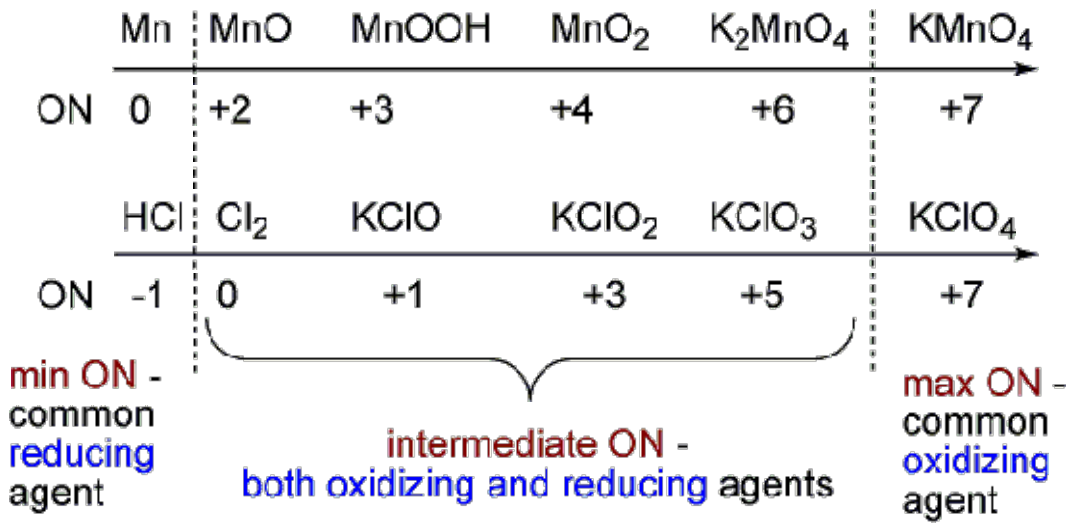


Figure 1.2. Effect of polyvalent element oxidation number (ON) on the redox properties of a substance containing this element

Some examples of redox reactions for above substances are follow:

- $Mn + Cl_2 \rightarrow MnCl_2$, Mn^0 – reductant, Cl^0 – oxidizer.
- $Cl_2 + 3F_2 \rightarrow 2ClF_3$, Cl^0 – reductant, F^0 – oxidizer.
- $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + H_2O$, Cl^-– reductant, Mn^{+4} – oxidizer.
- $3MnO_2 + KClO_3 + 6KOH \rightarrow 3K_2MnO_4 + KCl + 3H_2O$,

Mn^{+4} – reductant, Cl^{+5} – oxidizer.

- $3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KOH$,

auto-oxidation-reduction reaction or disproportionation.

- $Cl_2 + H_2O \rightarrow HCl + HClO$

auto-oxidation-reduction reaction or disproportionation.

- $2KMnO_4 + 5KClO_3 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5KClO_4 + K_2SO_4 + 3H_2O$,

Cl^{+5}– reductant, Mn^{+7} – oxidizer.

Redox ability of substances depends strongly on the pH of solutions as can be shown by potassium permanganate activity in different media. In acidic solution (pH < 7) Mn^{+7} accepts 5 electrons:

$$\begin{array}{l|l|l} MnO_4^- + 5e + 8H^+ \rightarrow Mn^{2+} + 4H_2O & 10 & \frac{2}{5} \\ SO_3^{2-} - 2e + H_2O \rightarrow SO_4^{2-} + 2H^+ & & \end{array}$$

$$2MnO_4^- + 16H^+ + 5SO_3^{2-} + 5H_2O \rightarrow$$

$$\rightarrow 2Mn^{2+} + 8H_2O + 5SO_4^{2-} + 10H^+$$

$$2MnO_4^- + 6H^+ + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Net reaction:

$2KMnO_4 + 5Na_2SO_3 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 3H_2O$.

In neutral solution (pH = 7) Mn^{+7} accepts 3 electrons:

$$\begin{array}{l|l|l} MnO_4^- + 3e + 2H_2O \rightarrow MnO_2 + 4OH^- & 6 & \frac{2}{3} \\ SO_3^{2-} - 2e + H_2O \rightarrow SO_4^{2-} + 2H^+ & & \end{array}$$

$$2MnO_4^- + 4H_2O + 3SO_3^{2-} + 3H_2O \rightarrow$$

$$\rightarrow 2MnO_2 + 3SO_4^{2-} + 8OH^- + 6H^+$$

$$2MnO_4^- + H_2O + 3SO_3^{2-} \rightarrow 2MnO_2 + 3SO_4^{2-} + 2OH^-$$

Net reaction: $2KMnO_4 + 3Na_2SO_3 + H_2O \rightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH$.

In alkali solution (pH > 7) Mn^{+7} accepts only 1 electron:

$$\begin{array}{l|l|l} MnO_4^- + e \rightarrow MnO_4^{2-} & 2 & \frac{2}{1} \\ SO_3^{2-} - 2e + 2OH^- \rightarrow SO_4^{2-} + H_2O & & \end{array}$$

$$2MnO_4^- + 2OH^- + SO_3^{2-} \rightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O$$

Net reaction: $2KMnO_4 + Na_2SO_3 + 2KOH \rightarrow 2K_2MnO_4 + Na_2SO_4 + H_2O$.

In general, for aqueous solutions, redox reactions balancing involves adding H^+, OH^-, H_2O, and electrons to compensate the changes in ionic composition and charges according to the Table 1.1.

Table 1.1 – Rules for ionic balancing of redox reactions

Medium	Donor of $[O^{-2}]$	Acceptor of $[O^{-2}]$
Acidic, H^+, H_2O	$H_2O \rightarrow [O^{-2}] + 2H^+$	$[O^{-2}] + 2H^+ \rightarrow H_2O$
Neutral, H_2O	$H_2O \rightarrow [O^{-2}] + 2H^+$	$[O^{-2}] + H_2O \rightarrow 2OH^-$
Alkali, OH^-, H_2O	$2OH^- \rightarrow [O^{-2}] + H_2O$	$[O^{-2}] + H_2O \rightarrow 2OH^-$

Concentration of substance is the factor of its redox activity, for example, in diluted sulfuric acid H^+ ions are the oxidizing agents, but in concentrated acid oxidizer changes for S^{+6}:

$$H_2SO_{4(diluted)} + Zn \rightarrow ZnSO_4 + H_2$$
$$5H_2SO_{4(concentrated)} + 4Zn \rightarrow 4ZnSO_4 + H_2S + 4H_2O$$
$$H_2SO_{4(diluted)} + Cu \rightarrow$$
$$2H_2SO_{4(concentrated)} + Cu \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Dilute and concentrated nitric acid also exhibit different behavior:

$$10HNO_{3(diluted)} + 4Zn \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$
$$4HNO_{3(concentrated)} + Zn \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$
$$8HNO_{3(diluted)} + 3Cu \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$4HNO_{3(concentrated)} + Cu \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

As well as the temperature is the instrument to control redox reactions:

$$HNO_{3(cool)} + Al \rightarrow Al_2O_3 \downarrow - \text{passivation}$$
$$6HNO_{3(hot)} + Al \rightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O$$

An oxidant and reductant which appear on opposite sides of a half-equation constitute a redox couple, for example, Fe^{2+}/Fe^{3+}:

$$Fe^{3+} + e \rightarrow Fe^{2+}.$$

Each redox couple or a half-reaction occurring in this couple has a standard redox potential $E°$:

$$E^0_{\text{red/ox}} = -\Delta G / zF,$$

where red – reduced form of particle (Fe^{2+});

ox – oxidized form of particle (Fe^{3+});

ΔG – change in free energy ;

z – a number of gaining or loosing electrons;

F – Faraday number, $1F = 96495Q \cdot \text{mol}^{-1}$

$$E^0_{Fe^{2+}/Fe^{3+}} = +0.77 \text{ V}.$$

Standard half-cell potential summarizes the relative power of a substance to donate or accept electrons. The greater the value of $E°$, the greater the tendency of the substance to give away electrons, and thus the stronger this substance is as an oxidant. The lower the value of $E°$, the greater the tendency of the substance to donate electrons and thus the stronger this substance is as a reductant.

Change in free energy of redox reaction is expressed as:

$$\Delta G^0 = - zF\Delta E^0,$$

where $\Delta E^0 = E_{ox} - E_{red}$; E_{ox} – the potential of oxidant reducing; E_{red} – the potential of reductant oxidizing.

It is necessary to compare the redox potentials of half-reactions in order to conclude about spontaneity and the possibility of the reaction. For example, copper is oxidized with nitric acid:

$$8HNO_{3(diluted)} + 3Cu \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu - 2e \rightarrow Cu^{2+} \qquad E^0_{Cu^{2+}/Cu^0} = +0.34\ V$$

$$NO_3^- + 3e + 4H^+ \rightarrow NO + 2H_2O \qquad E^0_{NO_3^-/NO} = +0.89\ V$$

$$E^0_{NO_3^-/NO} > E^0_{Cu^{2+}/Cu^0}$$

$$NO_3^- - \text{an oxidant};\ \ Cu - \text{a reductant}$$

but does not react with hydrochloric acid, as follows from the comparison of the metal redox potential and oxidative half reaction:

$$\text{but} \qquad HCl + Cu \rightarrow \text{no reaction}$$

$$2H^+ + 2e \rightarrow H_2 \qquad E^0_{2H^+/H_2} = 0.0\ V$$

$$\text{because} \quad E^0_{2H^+/H_2} < E^0_{Cu^{2+}/Cu^0}$$

1.2 CONTROL TASKS

1.2.1. Which of chemical particles given in Table. 2.1, have only oxidation or reduction properties or both?

Table 2.1 – Tasks variants

Variant	Chemical particles	Variant	Chemical particles
1	$KMnO_4$, MnO_2, V_2O_5, KI	13	Fe, Fe^{2+}, Si, $[SO_4]^{2-}$
2	PbO_2, HNO_3, N_2, H_2S	14	Cr^{3+}, $[Cr_2O_7]^{2-}$, O_2, Pb
3	Na_2SO_3, Be, NO, $K_2Cr_2O_7$	15	S, S^{2-}, $[SO_4]^{2-}$, K
4	HNO_3, $[GaO_2]^-$, N_2, Fe	16	Ga, Ga^{3+}, $Na_2Cr_2O_7$, Br_2
5	Sr, $HClO_4$, Mn^{2+}, ClO^-	17	$[NH_4]^+$, KNO_3, KCl, Na^+
6	In^{3+}, Mn, Pb^{2+}, PbO_2	18	MnO_2, Ag^+, N_2O, KI
7	Co, $Na_2Cr_2O_7$, Fe^{3+}, CO_2	19	$[SeO_4]^{2-}$, I_2, Hg, Fe_2O_3
8	$KClO_4$, Na_2S, Na_2O_2, Zn	20	$[NO_3]^-$, NO_2, HCl, N_2
9	B, H_2O_2, O_2, $[PO_4]^{3-}$	21	$[CO_3]^{2-}$, CH_4, V, V_2O_3
10	$[ClO_4]^-$, Cl_2, Al^{3+}, Al	22	CrO_3, MnO_2, $KGaO_2$, P
11	$[MnO_4]^{2-}$, F_2, Ag, Ti^{2+}	23	As, Be^{2+}, Sr, $[Al(OH)_4]^-$
12	Mg, Mg^{2+}, $[IO_3]^-$, I_2	24	K, BrO_3^-, F^-, $[Sn(OH)_4]^{2-}$

1.2.2. Choose the coefficients in the equations of oxidation-reduction reactions by electronic or electronic-ionic method for the variant (tab. 1.3). Determine the possibility of spontaneous course of reaction according to the values of the standard electrode potentials (Annex D)

Table 1.3 – Tasks variants

Variant	Schemes of oxidation-reduction reactions
1	$Na_2MoO_4 + HCl + Al \rightarrow MoCl_2 + AlCl_3 + NaCl + H_2O$
2	$FeSO_4 + KClO_3 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + KCl + H_2O$
3	$KCrO_2 + PbO_2 + KOH \rightarrow K_2CrO_4 + K_2PbO_2 + H_2O$
4	$Mn(NO_3)_2 + PbO_2 + HNO_3 \rightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$
5	$H_2SeO_4 + Au \rightarrow Au_2(SeO_4)_3 + SeO_2 + H_2O$
6	$ClO_2 + NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$
7	$HgS + HNO_{3(conc)} \rightarrow Hg(NO_3)_2 + H_2SO_4 + NO_2 + H_2O$
8	$I_2 + Cl_2 + H_2O \rightarrow HIO_3 + HCl$
9	$Cr_2(SO_4)_3 + Br_2 + NaOH \rightarrow Na_2CrO_4 + NaBr + Na_2SO_4 + H_2O$
10	$CrCl_2 + HNO_{3(concentrated)} \rightarrow Cr(NO_3)_3 + NO_2 + HCl + H_2O$
11	$KNO_2 + K_2Cr_2O_7 + HNO_3 \rightarrow KNO_3 + Cr(NO_3)_3 + H_2O$
12	$Cr_2O_3 + Na_2CO_3 + O_2 \rightarrow Na_2CrO_4 + CO_2$
13	$SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
14	$MnO_2 + NH_3 \rightarrow Mn_2O_3 + N_2 + H_2O$
15	$KI + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + I_2 + K_2SO_4 + H_2O$
16	$Zn + KMnO_4 + H_2SO_4 \rightarrow ZnSO_4 + MnSO_4 + K_2SO_4 + H_2O$
17	$H_2S + K_2Cr_2O_7 + H_2SO_4 \rightarrow SO_2 + K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
18	$Ni(OH)_2 + Cl_2 + KOH_{(conc)} \rightarrow NiO(OH) + KCl + H_2O$
19	$CrCl_3 + Br_2 + KOH \rightarrow K_2CrO_4 + KBr + KCl + H_2O$
20	$Sb_2O_3 + Br_2 + KOH \rightarrow KSbO_3 + KBr + H_2O$
21	$Mg + K_2Cr_2O_7 + H_2SO_4 = Cr_2(SO_4)_3 + MgSO_4 + K_2SO_4 + H_2O$
22	$NaCrO_2 + H_2O_2 + NaOH \rightarrow Na_2CrO_4 + H_2O$
23	$As + NaOH + NaClO \rightarrow Na_3AsO_4 + NaCl + H_2O$

1.3. EXPERIMENTAL PART

Experiment 1. Oxidative properties of substances

1.1. *Oxidizing properties of potassium dichromate*

Prepare in the test tube potassium dichromate solution acidified with sulfuric acid and add sodium sulfate (IV). Make a note of a color change of the reaction mixture. About what ions does this color indicate?

In two test tubes pour a solution of potassium dichromate acidified with concentrated sulfuric acid. Add by drops a solution of ethanol in the first test tube and a piece of zinc in the second. Observe the change in color of the reaction mixture in the two tubes.

1.2. *Oxidizing properties of potassium permanganate*

Pour into 3 test tubes 1–2 ml of potassium permanganate, in one pour in addition the same amount of dilute sulfuric acid, in the second – water, in the third – alkaline solution, and then add sodium sulfite. Observe the color change in each test tube. What is the oxidation state of manganese in each environment?

Conclude the nature of permanganate-ion reduction product depending on the pH basing on experiments. In what environment permanganate-ion has the highest oxidative activity?

1.3. *Oxidizing properties of lead (IV) oxide*

Add in a test tube some crystals of PbO_2, add diluted nitric acid and potassium iodide. Observe the appearance of the color. What substance adds the color to the solution?

1.4. *Oxidizing properties of halogens*

In the test tube add 3–4 drops of potassium iodide, gradually add 3–5 drops of perchloric water. What do you see? What is the function of iodide-ion and chlorine in these reactions?

1.5. *Oxidizing properties of oxygen*

By the exchange reactions get the residue of iron (II) hydroxide. Mix the that residue by a glass rod and observe after 1–2 min. browning of residue due to oxidation of iron (II) hydroxide to iron (III) hydroxide FeOOH. Write the equation of this reaction involving water molecules.

1.6. *Oxidizing properties of the iron (III) salts*

Add in the tube 2-3 drops of iron (III) sulfate and add the same amount of potassium iodide. Note the change of solution color that can be associated with the formation of free iodine. To identify iodine, dilute a few drops of the studied solution in a separate test tube by triple volume of water, and then add 2–3 drops of starch. What color has starch compound with formed iodine? Does the similar reaction Fe^{+3} with bromide ions proceed?

1.7. *Oxidizing properties of the copper (II) salts*

To 2–3 drops of copper (II) sulfate or chloride, add 1–2 drops of potassium iodide. Confirm as in the previous experiment, the formation of free iodine. Note that the residue formed is copper (I) iodide.

Experiment 2. Reductive properties of substances

2.1. *Reductive properties of metals*

Add in the test tube iodine water and put in it in a piece of magnesium. Observe the solution color becoming homogeneous. Write the reaction equation and do its thermodynamic analysis. Put in one test tube 1–2 pieces of zinc, in the second – iron, third – copper and add in each 5–6 drops of lead nitrate or acetate. In a few minutes will be seen a major formation of lead crystals that shine on the surface of metal pieces. In which case and why the exchange of electrons between metal and ions of metal metallic does not happen?

2.2. *Reductive properties of nitrogen in the oxidation state* (–3)

In the test tube, pour 1–2 ml of potassium permanganate, add a solution of ammonia and warm up until it changes the color of the

reaction mixture. Write the reaction equation, given that ammonia is oxidized to molecular nitrogen and potassium permanganate is reduced to manganese dioxide. Repeat the experiment, replacing the potassium permanganate on dichromate. Does the reaction occur in this case?

2.3. *Reductive properties of sulfur in the oxidation state* (–2)

In one test tube, pour 1–2 ml of potassium permanganate, which is acidified with dilute sulfuric acid solution and add ammonium sulfide. Observe reaction mixture becoming homogeneous.

In the second test tube to 2–3 ml of potassium dichromate, which is acidified with dilute sulfuric acid, add 4–5 ml of ammonium sulfide. Note the color of the reaction mixture and residue.

Experiment 3. Oxidation-reduction duality

3.1. *Redox duality of nitrites*

To 2–3 ml of potassium iodide, acidified with sulfuric acid, add 1–2 ml of sodium nitrate (III). What substances are formed? How has the color changed?

To 1–2 ml of potassium permanganate solution add 1–2 ml of dilute sulfuric acid, and then drop by drop add a solution of sodium nitrate (III) to complete bleaching of the solution.

What function prevails in nitrate (III) behavior – oxidative or reductive? Explain your response based on the values of oxidation-reduction potentials of the studied systems.

3.2. *Redox duality of hydrogen peroxide*

To 2–3 ml of potassium iodide add the same amount of dilute sulfuric acid, drop by drop add a solution of hydrogen peroxide. What substance will appear and how it can be found?

To 1–2 ml of potassium permanganate in acidic medium add a solution of hydrogen peroxide to complete bleaching of the solution. Pay attention to the evolution of gas and try it with smoldering torch. Explain which function prevails in the behavior of hydrogen peroxide.

CHAPTER 2 ELECTROCHEMICAL PROCESSES AND SYSTEMS

2.1 BASIC CONCEPTS AND DEFINITIONS

The electrochemical reaction is the heterogeneous redox reaction in which the chemical energy is converted to the electrical or *vice versa*. The chemical energy of spontaneous ($\Delta G < 0$) redox reaction may be converted directly into electricity when the oxidation half-reaction is spatially separated from the reduction one. Such systems are known as *chemical sources of energy* or *galvanic cells*. Nonspontaneous ($\Delta G > 0$) redox reaction may be realized under the action of electric current from outside source – the electric energy being converted to the chemical one. Such processes are known as electrolysis and the system to which electricity is supplied is called an *electrolytic cell*.

Each electrochemical system consists of three components:

- two separated electrodes – the electron conductive solid substances (metals or *n*-semiconductors);
- electrolyte – the ion conductive solution or melt;
- external circuit (metal wire) which connects electrodes with the souse or consumer of electric current.

In either kind of cell, the electrode at which *oxidation* occurs is called the *anode* and the electrode at which *reduction* occurs is the *cathode*:

- Chemical redox reaction:
  $Zn + CuSO_4 \rightarrow Cu + ZnSO_4$
- Electrochemical reaction:
  - anode: $Zn \rightarrow Zn^{2+} + 2e$;
  - cathode: $Cu^{2+} + 2e \rightarrow Cu$

Electrochemistry studies reactions in which charged particles (ions or electrons) cross the interface between two phases of matter:

- a metallic phase – the electrode and
- a conductive solution – electrolyte.

A process of this kind can be represented as a chemical reaction and is known generally as an electrode process. The transition region between two phases consists of a region of charge unbalance (Fig. 2.1) and is the double electric layer (DEL). It consists of an inner monomolecular layer of adsorbed H_2O and ions, and an outer diffuse region that compensates for any local charge unbalance that gradually merges into the completely random arrangement of the bulk solution. Electrode processes (electrode reactions) take place within the double electric layer. The interfacial potential difference which develops in electrode-solution systems is known as electrode potential and limited to only a few volts. This potential difference spans a very small distance which corresponds to a few atomic diameters (Fig. 2.2).

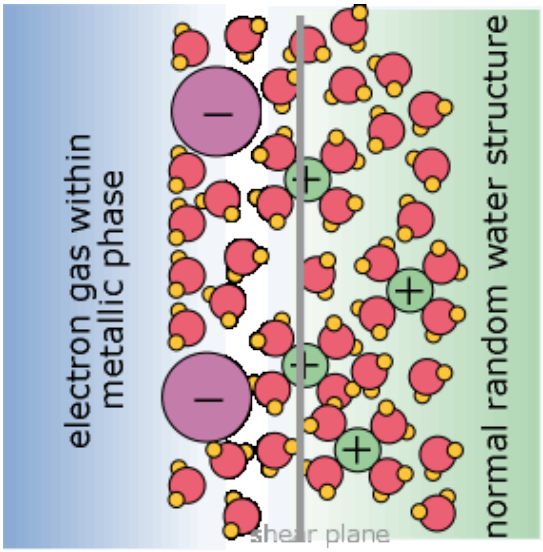


Figure 2.1. Structure of the double electric layer

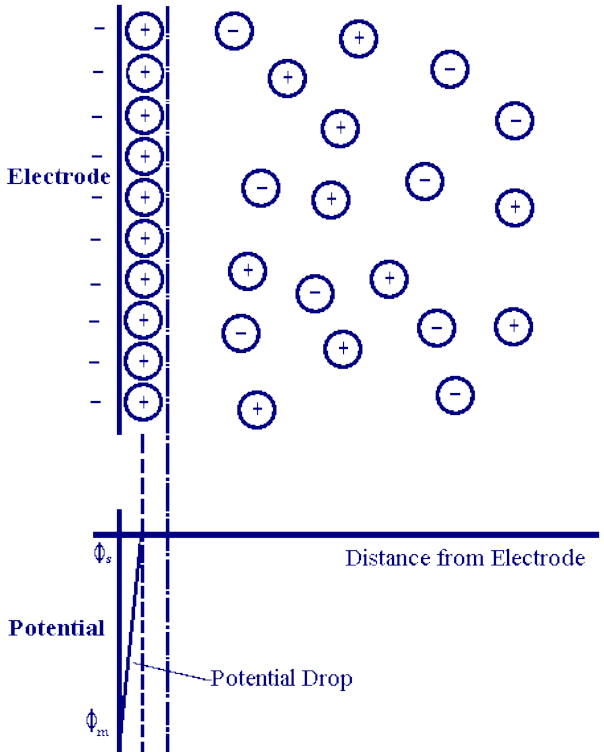


Figure 2.2. Electrode potential

In order to measure the relative potential of electrode couple M^{2+}/M, we can set up a cell Pt | $H_2(g)$ | H^+ || M^{2+} (aq) | M(s) (Fig. 2.3). The two half-cells are joined through the salt bridge in the middle. The potential difference between these electrodes will be $\Delta E = E_M - E_H$.

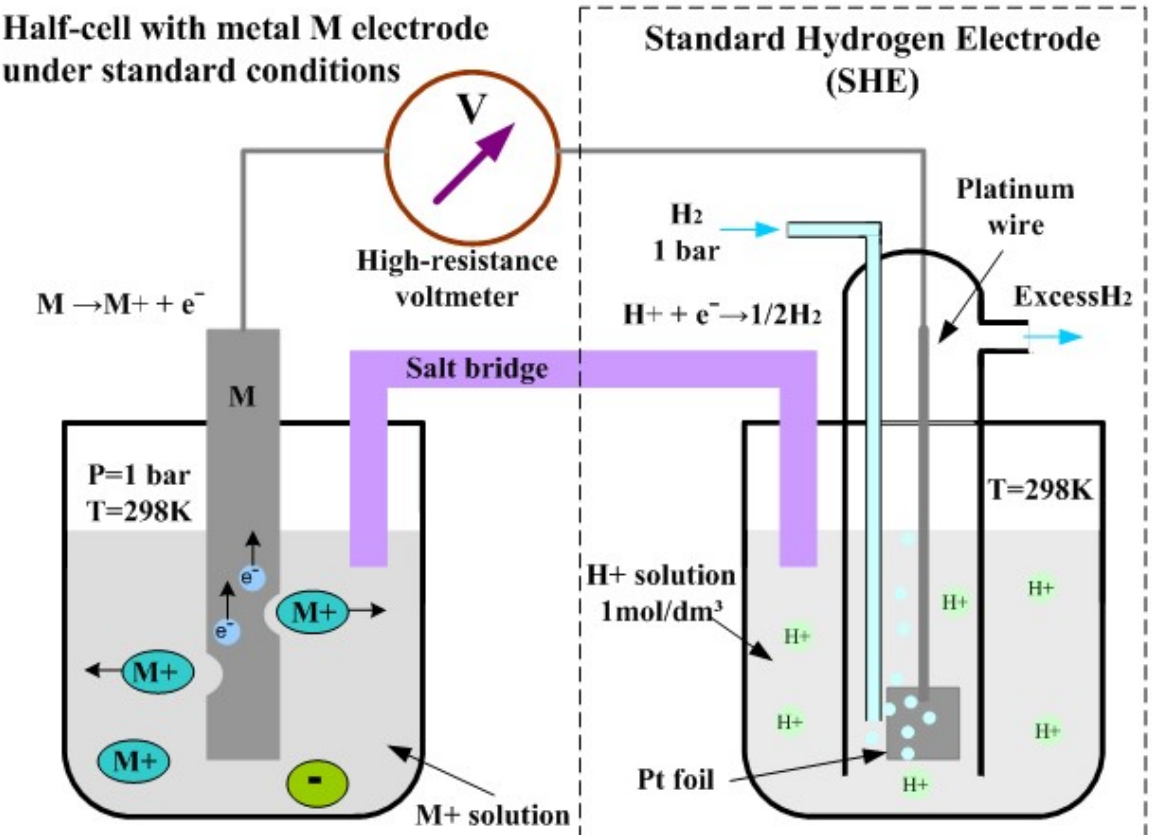


Figure 2.3. Scheme for measuring electrode potential

The universal reference cell is the hydrogen half-cell

$$Pt \mid H_2(g) \mid H^+(aq) \parallel ...,$$

in which H_2 is allowed to bubble over a Pt electrode having a specially treated surface which catalyzes the reaction:

$$H_2(g) \leftrightarrow 2H^+ + 2e.$$

When this electrode is operated under standard conditions of 1 atm (101325 Pa) H_2 pressure, 25 °C (298 K), and pH 0, it becomes the standard hydrogen electrode sometimes abbreviated SHE. Potential of this electrode means to be $E_H = 0$ V.

The difference between the electrodes potentials is a measure of the tendency for the cell reaction to take place. The more positive the half-cell potential, the greater is the tendency for the reduction reaction to proceed. The more negative the half-cell potential, the greater is the tendency for the oxidation reaction to proceed. The difference of half-cell potentials is known as electromotive force

$$\Delta E^0 = E_{\text{cathode}} - E_{\text{anode}},$$

and is related to the standard free energy change:

$$\Delta G^0 = -zF\Delta E^0.$$

The standard potential refers to cells in which all dissolved substances are at unit concentration of 1M; gases that take part in an electrode reaction are at an effective pressure of 1 atm (101325 Pa); temperature is 298 K. Nernst equation relates the equilibrium potential to the standard potential and to the concentration of the electro-active species $c(M^{n+})$. For half reaction: $M^{n+} + ne \rightarrow M^0$ equilibrium potential may be calculated using approach:

$$E_{\mathrm{M}^{z+}/\mathrm{M}} = E^0_{\mathrm{M}^{z+}/\mathrm{M}} + \frac{RT}{zF}\ln c_{\mathrm{M}^{z+}},$$

if we consider, that $\ln X = 2.3\lg X$, $RT/F = 0.059$, we can transform the equation to the form:

$$E_{\mathrm{M}^{z+}/\mathrm{M}} = E^0_{\mathrm{M}^{z+}/\mathrm{M}} + \frac{0{,}059}{z}\lg c_{\mathrm{M}^{z+}}$$

Stability of water may be described in terms of electrochemical processes. Water is subject to decomposition by strong oxidizing agents such as F_2 or Cl_2 and by reducing agents stronger than H_2. The reduction half reaction in acidic solution:

$$2H_3O^+ + 2e \rightarrow H_2(g) + H_2O,$$

or, in neutral or alkaline solutions

$$2H_2O + 2\,e \rightarrow H_2(g) + 2OH^-.$$

These two reactions are equivalent and follow the same Nernst equation:

$$E_{2H^+/H_2} = E^0_{2H^+/H_2} + 2.3\frac{RT}{nF}\log\frac{c^2_{H_2}}{P_{H_2}}$$

which, at 25 °C and unit H_2 partial pressure reduces to

$$E = E_0 - (0.059/2)\cdot 2\,\mathrm{pH} = -0.059\,\mathrm{pH}$$

Similarly, the oxidation of water in acidic solution and neutral solutions:

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e,$$

in alkaline solution:

$$4OH^- + \rightarrow O_2(g) + 2H_2O + 4e,$$

is governed by the Nernst equation

$$E_{O_2/H_2O} = E^0_{O_2/H_2O} + 2.3\frac{RT}{nF}\log(P_{O_2}c^4_{H^+}),$$

which similarly becomes $E = 1.23 - 0.059$ pH.

So, the *E-vs*-pH plots (Fig. 2.4) for both processes have identical slopes and yield the stability diagram for water.

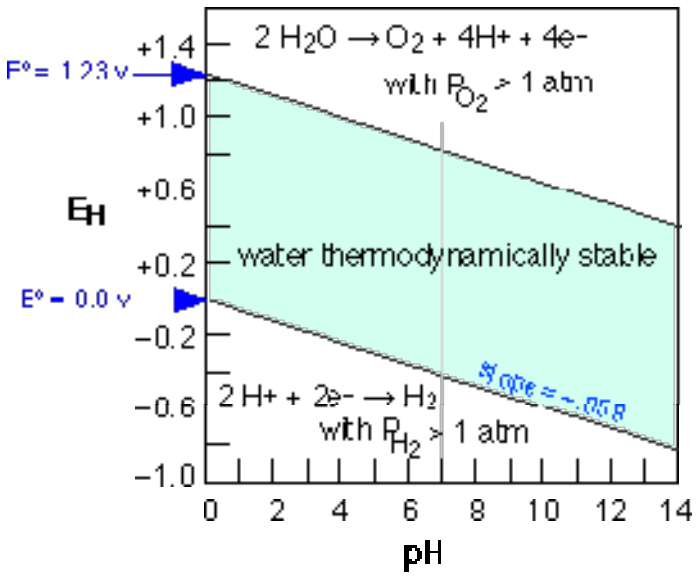


Figure 2.4. Stability diagram for water (Pourbaix diagram)

Galvanic cells. A special symbolic notation of the typical galvanic cell (Daniel cell) is following:

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s).$$

The single vertical bars represent phase boundaries. The double bar denotes a liquid–liquid boundary which in laboratory cells consists of a salt bridge or in ion-permeable barrier (Fig. 2.5).

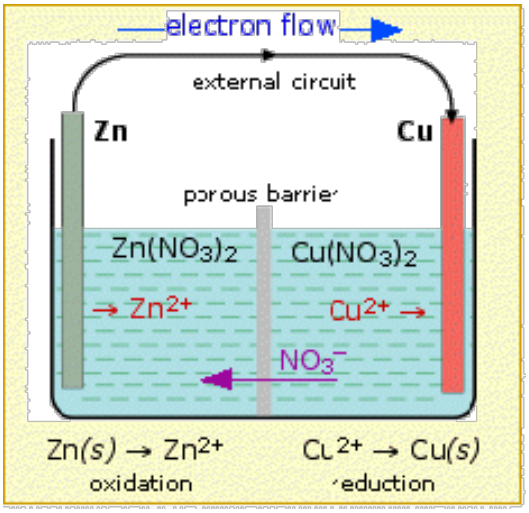


Figure 2.5. Typical galvanic cell – Daniel cell

During the cell work the mass of cathode increases, but the concentration of Cu^{2+} ions decreases; the mass of anode decreases, and the concentration of Zn^{2+} ions increases. The electromotive force (*emf*) of the cell may be calculated as:

$$emf = E^0(Cu^{2+}/Cu) - E^0(Zn^{2+}/Zn);\ emf = 0.34 - (-0.76) = 1.1\ V.$$

2.2 ELECTROCHEMICAL ENERGY STORAGE AND CONVERSION

A *secondary* or *storage battery* is capable of being recharged; its electrode reactions can proceed in either direction. During charging, electrical work is done on the cell to provide the free energy needed to force the reaction in the non-spontaneous direction. A *primary cell* (an ordinary flashlight battery) cannot be recharged with any efficiency, so the amount of energy it can deliver is limited to that obtainable from the reactants that were placed in it at the time of manufacture.

Some examples of commercial cells and batteries are following.

In the *LeClanché "dry cell"* of construction given at Fig. 2.6, which may be represented by scheme

$$Zn(s) \mid NH_4Cl(s) \parallel MnO_2(s) \mid (C)(s),$$

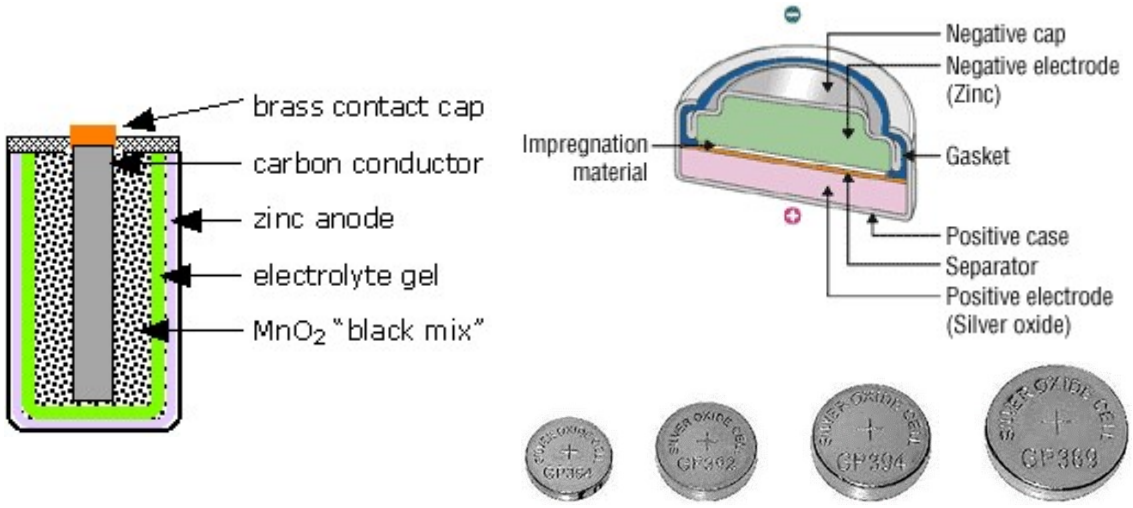
the electrode reactions are

Anode: $Zn + 2NH_4^+ \rightarrow [Zn(NH_3)_2]^{2+} + 2H^+ + 2e$;

Cathode (C): $MnO_2 + H^+ + e \rightarrow MnOOH$;

Net reaction is $Zn + 2MnO_2 + 2NH_4Cl \rightarrow [Zn(NH_3)_2]Cl_2 + 2MnOOH$.

The electrolyte is a wet paste containing NH_4Cl to supply the H^+ ions. There are many side reactions and these cells have limited shelf-life due to self-discharge: $Zn + 2NH_4^+ \rightarrow [Zn(NH_3)_2]^{2+} + H_2$. The *emf* of such cell is of 1.45-1.55 V, and energy density reaches 30-50 watt-hour/kg.



a *b*

Figure 2.6. Construction of LeClanché "dry cell" (a) and silver-zinc alkaline cell (b)

Silver-zinc alkaline cell is characterized by larger shelf-life, efficiency and specific parameters. The scheme of the cell is

$$Zn(s) \mid KOH(gel) \mid Ag_2O(s)\ (Ag)(s).$$

The electrode reactions are

Anode: $Zn + 4OH^- \rightarrow ZnO_2^{2-} + 2H_2O + 2e$;

Cathode: $Ag_2O + H_2O + 2e \rightarrow 2Ag + 2OH^-$;

Net reaction: $Zn + Ag_2O + 2KOH \rightarrow K_2ZnO_2 + 2Ag + H_2O$.

The *emf* of such cell is higher than LeClanché 1.55 –1.8 V, and energy density reaches 80–110 watt-hour/kg.

The *lead-acid storage cell* (Fig.2.7 a). The most well-known storage cell is the lead-acid cell, which was invented by Gaston Planté in 1859 and is still the most widely used device of its type.

The cell is: $Pb(s) \mid H_2SO_4(aq)\ (5\ M) \mid PbO_2(s) \mid Pb(s)$

Anode: $Pb + SO_4^{2-} \leftrightarrow PbSO_4 + 2e$

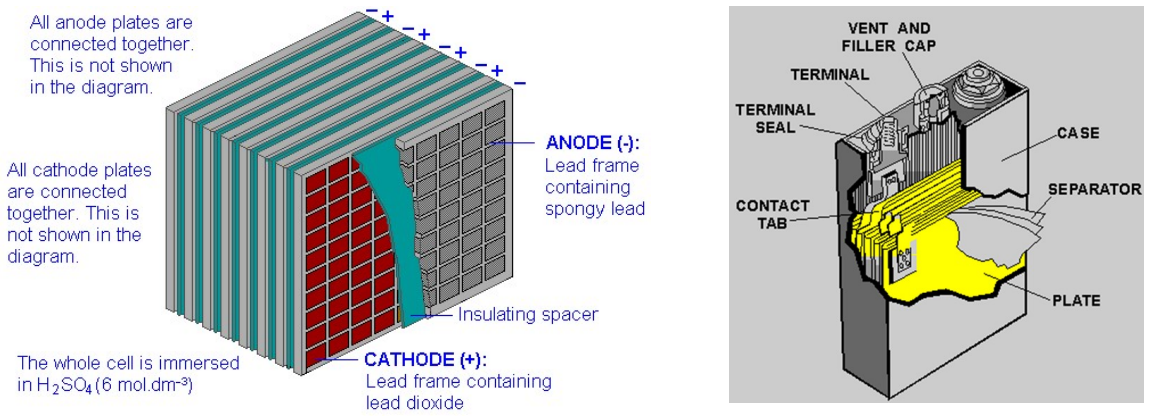
Cathode: $PbO_2 + 2e + 4H^+ + SO_4^{2-} \leftrightarrow PbSO_4 + 2H_2O$

the net cell reaction is

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \leftrightarrow 2PbSO_4(s) + 2H_2O$$

The *emf* of such cell is 2.041 V; energy density is of 5–40 watt-hour/kg. They can deliver 300-500 of charge–discharge cycles. The temperature range is of T = –30 – +40 °C.

The advantages of these batteries are trend to slowly self-discharge. But re-crystallized $PbSO_4$ does not get converted to PbO_2 which limits the battery capacity. "Fast" charging causes rapid evolution of H_2 from the water in the electrolyte; the bubbles form on the lead surface and can tear PbO_2 off the positive plate.



a b

Figure 2.7. Construction of acid (a) and alkaline battery (b)

Nickel-iron alkali battery Ni-Fe (Fig.2.7 b).

Fe*(s)* | KOH*(ag)* | NiOOH(s), Ni*(s)*

The electrode reactions are

Anode: $Fe + 2OH^- \leftrightarrow Fe(OH)_2 + 2e$

Cathode: $NiOOH + H_2O \leftrightarrow Ni(OH)_2 + OH^- + e$

Net reaction: $Fe + 2NiOOH + 2H_2O \leftrightarrow Fe(OH)_2 + 2Ni(OH)_2$

Quantitative characteristics of batteries:

- The *emf* – 1.48 V;
- Energy density – 25 – 30 watt-hour/kg;
- They can deliver 750-1000 of charge–discharge cycles;
- Operating temperature T = –50 – +50 °C.

A metal-hydride battery operating is shown in Fig.2.8.

MH(g) Pt| KOH*(ag)* | NiOOH(s), Ni*(s),*

where MH – metal (Ti, Zr, Mg, La, Ce)

The electrode reactions are:

Anode: $MH + OH^- \leftrightarrow M + H_2O + e$;

Cathode: $NiOOH + H_2O \leftrightarrow Ni(OH)_2 + OH^- + e$.

Net reaction: $MH + NiOOH \leftrightarrow Ni(OH)_2 + M$.

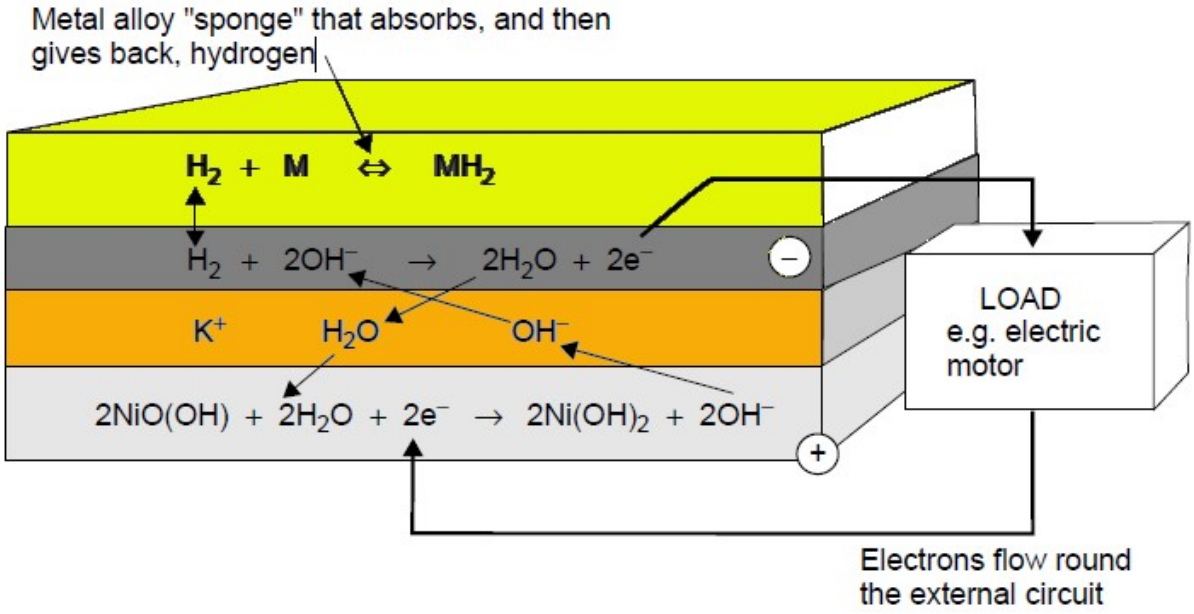


Figure 2.8. Metal-hydride batteries operating

Quantitative characteristics of batteries:

- The *emf* – 1.45-1.5 V;
- Energy density – 80 watt-hour/kg;
- They can deliver 1000 of charge–discharge cycles.

Lithium-ionic batteries: Li_xC_6 | $LiAlF_4$ | Li_xCoO_2 (Fig.2.9).

The positive electrode (cathode) half-reaction in the lithium-doped cobalt oxide substrate is:

$$CoO_2 + Li^+ + e \leftrightarrow LiCoO_2.$$

The negative electrode (anode) half-reaction for the graphite is:

$$LiC_6 \leftrightarrow C_6 + Li^+ + e.$$

The net reaction (left to right: discharging, right to left: charging) being:

$$CoO_2 + LiC_6 \leftrightarrow C_6 + LiCoO_2.$$

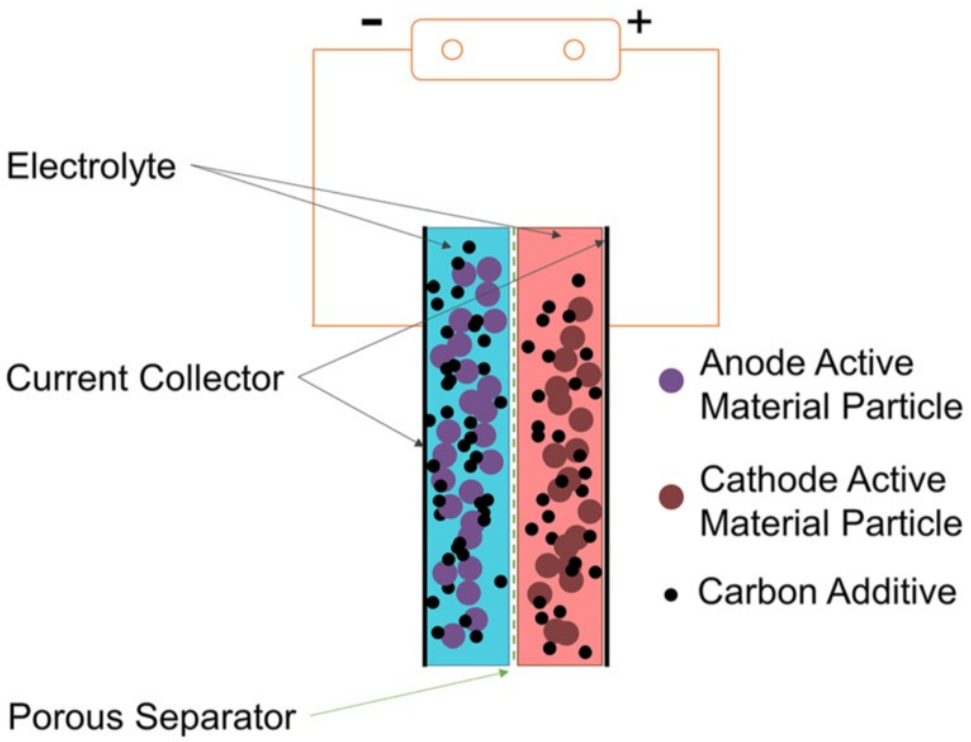


Figure 2.9. Lithium battery

In a lithium-ion battery the lithium ions are transported to and from the positive or negative electrodes by oxidizing the transition metal, cobalt (Co), in $Li_{1-x}CoO_2$ from Co^{3+} to Co^{4+} during charge, and reducing from Co^{4+} to Co^{3+} during discharge.

Quantitative characteristics of batteries:

- The *emf* – 3.5–3.7 V;
- Energy density – 150–500 watt-hour/kg;
- They can deliver 500–1000 of charge–discharge cycles;
- T = –40 – +60 °C.

Fuel cell is the most environment friendly device (Fig. 2.10).

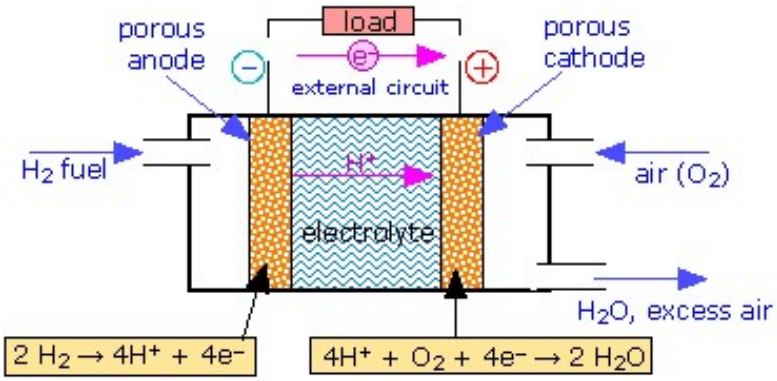
The cell reaction is the production of water from H_2 and O_2. H_2 enters the cell through a porous carbon electrode which also contains a Pt catalyst. O_2 is supplied to a similar electrode, the catalyst is Ag. The electrolyte is usually a warm solution of KOH.

The electrode reactions:

Anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e$

Cathode: $O_2(g) + 2H_2O + 4e \rightarrow 4OH^-(aq)$

Net reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O$



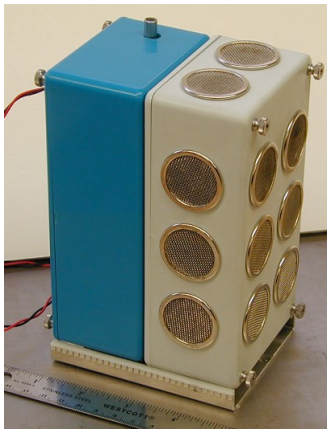


Figure 2.10. Fuel cell

This fuel cell will continue to operate and produce electrical energy as long as a supply of H_2 and O_2 are available. While an internal-combustion engine is only about 25 % efficient and a steam engine about

35 % efficient, the $H_2 – O_2$ cell just described can already operate at an efficiency of 45 %. Because of this high efficiency many possible uses and developments for fuel cells have been proposed.

Large nuclear power plants floating on the sea produce H_2 by the decomposition of H_2O rather than producing electrical power. This hydrogen gas could then be piped to individual homes where it could either be burned for heat or converted to electricity with the aid of a fuel cell. Automobiles powered by cells fueled by conventional gasoline or perhaps H_2. These automobiles would run virtually noiselessly without any pollution problems and deliver twice as many kilometers per liter of fuel as a conventional vehicle.

2.3 ELECTROLYTIC CELLS

When an electrical current flow through matter, permanent chemical changes often occur. In some cases, electrical energy supplied from an outside source can cause a chemical reaction to take place. Such a process is called electrolysis, and the system to which electricity is supplied is called an electrolytic cell. Electrolytic cells have numerous commercial applications:

- Chlorine, sodium hydroxide, hydrogen, aluminum, magnesium, sodium, calcium, and high-purity copper are some of the more important chemicals produced by electrolysis.
- Electro-plating of metals such as chromium, silver, nickel, zinc, and tin is also quite important.

Electrolysis of the molten sodium chloride

A source of direct current is connected to a pair of inert electrodes immersed in molten NaCl which is dissociated:

$$NaCl \rightarrow Na^+ + Cl^-;$$

Na+ ions flow toward the negative electrode and the Cl^- ions flow toward the positive electrode (Fig.2.11). The electrode reactions are:

Cathode (–): $Na^+ + e \rightarrow Na$

Anode (+): $2\ Cl^- \rightarrow Cl_2 + 2e$

Net reaction: $2\ NaCl(l) \rightarrow Cl_2(g) + 2\ Na(l)$

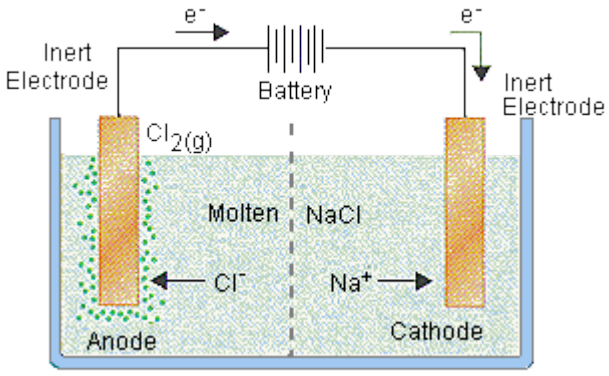


Figure 2.11. Electrolytic cell for electrolysis of molten NaCl

Commercial Downs cell

Gas Cl_2 that forms on the graphite anode inserted into the bottom of the cell bubbles through the molten NaCl into a funnel at the top (Fig.2.12).

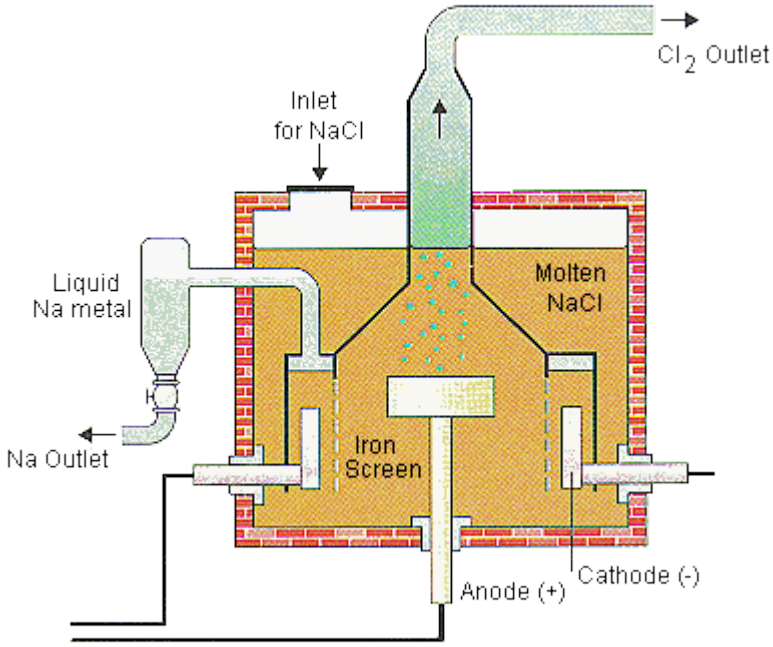


Figure 2.12. Commercial Downs cell

Metallic sodium Na forms at the cathode floats up through the molten sodium chloride into a sodium-collecting ring, from which it is periodically drained. The diaphragm that separates the two electrodes is

a screen of iron gauze, which prevents the contact of the electrolysis products. The mixture 3:2 by mass of $CaCl_2$ and NaCl is used because it has a melting point (mp) of 580 ºC, whereas pure NaCl mp is more than 800 ºC.

Electrolysis of the sodium chloride solution differs from the melting salt ones. In water solution there are water molecules in which hydrogen ions are stronger oxidizing agents compared with Na^+ ions:

$$NaCl \rightarrow Na^+ + Cl^-, H_2O.$$

The cathode reaction will be:

$$2H_2O + 2e \rightarrow H_2 + OH^-,$$

because $E^0_{H_2O/H_2}(pH\,7) = 0.413\,V > E^0_{Na^+/Na} = 2.71\,V.$

Anodic reaction will be the chloride ions oxidation accompanied with oxygen evolution:

$$2Cl^- \rightarrow Cl_2 + 2e\ (90\%),\ [2H_2O \rightarrow O_2 + 4H^+ + 4e\ (10\ \%)],$$

because $E^0_{H_2O/O_2}(pH\,7) = +0.817\,V\,;\, E^0_{Cl_2/2Cl^-} = +1.36\,V.$

Net reaction: $2NaCl(aq) + H_2O \rightarrow Cl_2(g) + 2NaOH(aq) + H_2(g)$

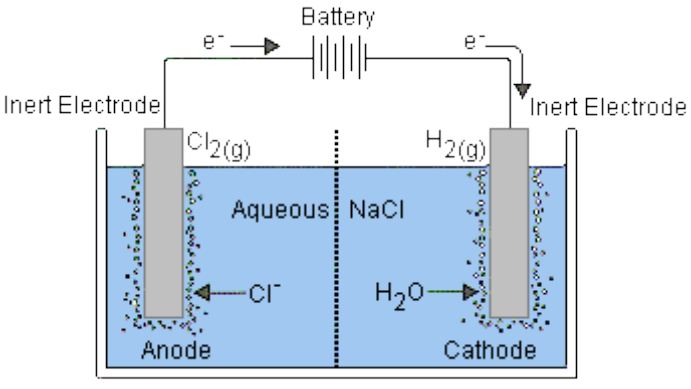


Figure 2.12. Electrolytic cell for electrolysis of NaCl solution

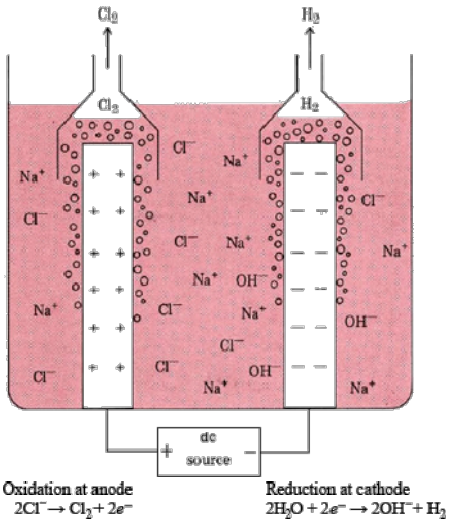


Figure 2.13. Hooker cell

From E^0 it would seem easier to oxidize H_2O, but the cell is never allowed to reach standard-state conditions. The solution is typically 25 % NaCl by mass, which significantly decreases the potential required to oxidize the Cl- ion. The products of the electrolysis react to form sodium hypo-chlorite, which is the first step in the preparation of hypochlorite bleaches, such as Chlorox:

$$Cl_2(g) + 2OH^- (aq) \rightarrow Cl^- (aq) + OCl^-(aq) + H_2O(l).$$

Rules for electrolysis

The mode of electrode reactions depends on the ionic composition of electrolyte, nature of solvent and nature of electrode. Cathode reaction: in water solution of different ionic composition the stronger oxidizing agent (with higher redox potential) will reducing at the cathode in the first place: Ag^+, Cu^{2+}, Ni^{2+}, Zn^{2+}

Anode reaction: in water solution of different ionic composition the stronger reducing agent (with lower redox potential) will oxidizing at the anode in the first place: I^-, Br^-, Cl^-.

Rules for electrolysis of water solutions: cation nature influence

The cations of metal disposing before Ti in the standard electrode potential range (SEPR) have no capability for reduction at the cathode in water presence (Table 2.1). The cations of metal disposing between Ti and H in the SEPR are reduced at the cathode simultaneously with water.

Table 2.1 – Cathodic reactions

Li^+, …, Ti^{3+}	Mn^{2+}, …, H^+	W^{2+}, …, Au^{3+}
$2H_2O + 2e \rightarrow H_2 + 2OH^-$	$M^{n+} + ne \rightarrow M$ $2H_2O + 2e \rightarrow H_2 + 2OH^-$	$M^{n+} + ne \rightarrow M$
Inert electrodes: C, Pt, stainless steel	Both inert and active anodes. Active anode: $M \rightarrow M^{n+} + ne$	

Rules for electrolysis of water solutions at inert anode: anion nature influence

The anodic reaction at inert electrodes strongly depends on the ionic composition of the solution (Table 2.2). Firstly, OH^--ions are oxidizing at the anode in alkali solutions. Oxygen containing anions with the largest oxidation number of central elements have no capability for oxidation at the anode in water presence.

Table 2.2 – Anodic reactions

Cl^-, Br^-, I^-, S^{2-}, NO_2^-, SO_3^{2-}, PO_3^{3-}, …	OH^-	ClO_4^-, CrO_4^{2-}, NO_3^-, SO_4^{2-}, PO_4^{3-}, MnO_4^-, …
$2Hal^- \rightarrow Hal_2 + 2e$ *or* $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e$	$4OH^- \rightarrow O_2 + 2H_2O + 4e$	$2H_2O \rightarrow O_2 + 4H^+ + 4e$

Examples of sodium sulfate and hydroxide electrolysis.

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}, H_2O$$
$$\text{cathode}: 2H_2O + 2e \rightarrow H_2 + 2OH^- \mid 2$$
$$\text{anode}: \quad 2H_2O \rightarrow O_2 + 4H^+ + 4e \mid 1$$
$$6H_2O \rightarrow 2H_2 + [4OH^- + 4H^+] + O_2$$
$$\text{net reaction}: 2H_2O \rightarrow 2H_2 + O_2$$

$$NaOH \rightarrow Na^+ + OH^-, H_2O$$
$$\text{cathode}: 2H_2O + 2e \rightarrow H_2 + 2OH^- \mid 2$$
$$\text{anode}: \quad 4OH^- \rightarrow O_2 + 2H_2O + 4e \mid 1$$
$$4H_2O + [4OH^-] \rightarrow 2H_2 + [4OH^-] + O_2$$
$$\text{net reaction}: 2H_2O \rightarrow 2H_2 + O_2$$

The laboratory preparation of $H_2(g)$ and $O_2(g)$ by passing electrical current through water solution in the cell containing sodium sulfate or sodium hydroxide (to support high conductivity of the electrolyte) and inert electrodes. The volume of produced at the cathode $H_2(g)$ is twice larger than a volume of produced at the anode $O_2(g)$

Aluminum production

Al is easily oxidized and so Al_2O_3 is difficult to reduce. Water is reduced rather than $Al^{3+}(aq)$, and electrolysis must be carried out in a

molten salt. Even this is difficult because the melting point of Al_2O_3 is above 2000 °C – a temperature which is very difficult to maintain. It was developed in 1886 by Charles Hall that in cryolite Na_3AlF_6 the Al_2O_3 can be dissolved at just over 1000°C. The electrolytic cell used for the Hall process consists of a steel box lined with graphite (Fig.2.14). This contains the molten Na_3AlF_6 and Al_2O_3 and also serves as the cathode. The anode is a large cylinder of carbon.

Passage of electrical current maintains the high temperature of the cell and causes the half-reactions to occur:

Cathode: $Al^{3+} + 3e \rightarrow Al(l)$

Anode: $2O^{2-} + C(s) \rightarrow CO_2(g) + 4e$

Since the anode is consumed by the oxidation half-equation, it must be replaced periodically.

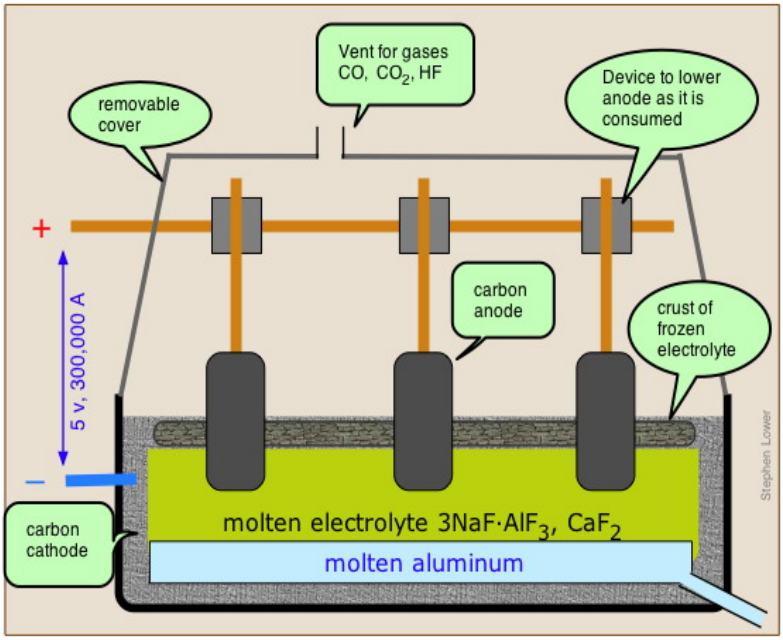


Figure 2.14. The electrolytic cell used for the Hall process

Aluminum production requires vast quantities of electrical energy, both to maintain the high temperature and to cause half-reactions to occur. Currently about 5 % of the total electrical energy produced in the United States goes into the Hall process. Several other easily oxidized metals are currently produced by electrolysis, but not in such large

quantities as Al. Mg is obtained by electrolyzing molten $MgCl_2$ which is derived from seawater. Na and Ca are produced together from a molten mixture of NaCl and $CaCl_2$.

Electrolytic purification of copper

Even small concentrations of impurities noticeably lower copper's electrical conductivity. Such a high degree of purity can be obtained by electrolytic refining. A thin sheet of high-purity Cu serves as the cathode, and the anode is the impure Cu which is to be refined. The electrolyte is a solution of $CuSO_4$. Some of the impurities are metals: Fe and Zn which are more easily oxidized than Cu. When current passes through the cell, these impurities go into solution from the anode, along with Cu:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e;\ Fe(s) \rightarrow Fe^{2+}(aq) + 2e;\ Zn(s) \rightarrow Zn^{2+}(aq) + 2e$$

All ions migrate toward the cathode, but $Cu^{2+}(aq)$ is more readily reduced than $Fe^{2+}(aq)$ or $Zn^{2+}(aq)$ and so it is the only one that plates out:

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s).$$

The impurity ions remain in solution. Other impurities, such as Ag, Au, and Pt, are less easily oxidized than Cu. These remain in metallic form and fall to the bottom of the cell, forming "anode sludge" from which they can later be recovered. The great value of Ag, Au, and Pt helps to offset the cost of refining.

Electroplating

An important industrial application of electrolysis is the plating of one metal on top of another. A typical example is the bumper of a car. This is made from steel and then plated with a thin layer of chromium to make it resistant to rusting and scratching.

Many other metal objects, such as pins, screws, watchbands, and doorknobs, are made of one metal with another plated on the surface. The object to be plated is used as the cathode, and the electrolyte contains some ionic compound of the metal to be plated. As current

flows, this compound is reduced to the metal and deposits on the surface of the cathode. The active anode in common case is the metal to be plated to support the stable concentration of its ions in electrolyte.

Nickel coating on the steel (Fig.2.15 a)

As electrolyte is used $NiSO_4$ and some components to obtain high conductivity of the solution, uniform and glitter coating. A sheet of pure nickel is an anode (Fig.2.15 b). Some Cl^- ions containing compounds are added to the electrolyte to prevent the anode passivation. Electrode reactions occurring when current passes through the cell are follows:

Cathode (steel): $Ni^{2+}(aq) + 2e \rightarrow Ni(s)$, C_e = 85-90 %;

$2H_2O + 2e \rightarrow H_2(g) + 2OH^-$, C_e = 15-10 %;

Anode (Ni): $Ni(s) \rightarrow Ni^{2+}(aq) + 2e$.

There is no net reaction in such case.

a b

Figure 2.15. Nickel coating electrodeposition

Quantitative aspects of electrolysis: Faraday laws

The amount of a substance consumed or produced at one of the electrodes in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell. One coulomb of charge is transferred when a 1 Amp current flows for 1 second: 1 C = 1 Amp·s.

For single reaction at electrode $\Delta m = \frac{M}{nF} It$;

For parallel reactions at electrode $\Delta m = \frac{M}{nF} ItC_e$,

where C_e - current efficiency that indicates the part of whole current corresponding to a partial reaction.

If gas is educing in electrode reaction the Faraday law may be following.

For single reaction at electrode $\Delta V = \frac{V}{nF} It$;

For parallel reactions at electrode $\Delta V = \frac{V}{nF} ItC_e$,

where C_e - current efficiency that indicates the part of whole current corresponding to a partial reaction.

Determination of technologic parameters for metal electroplating process:

$\Delta m = \rho \delta S$,

where ρ - a metal density, gm^{-3};

δ - a thickness of metal coating, m;

S - an area of metal surface, m^2;

taking into account that $I / S = j$ - current density, Am^{-2};

$$\delta = \frac{M}{nF\rho} jtC_e.$$

2.4 CONTROL TASKS

2.4.1. Make a scheme of galvanic cell from electrodes given in the Table 2.3:

- Write anodic and cathodic reactions and net process reaction.
- How do the masses of anode and cathode change during the galvanic cell processing?
- What is the direction of electron flow in external circuit?
- Calculate the electromotive force of galvanic cell.

Table 2.3 − Variant of problem

Variant	Electrodes	Variant	Electrodes
1	Cd^{+2}/Cd; Cu^{+2}/Cu	10	Mn^{+2}/Mn; Bi^{+3}/Bi
2	Fe^{+2}/Fe; Ag^{+}/Ag	11	Cd^{+2}/Cd; Hg^{+2}/Hg
3	Sn^{+2}/Sn; Al^{+3}/Al	12	Cr^{+3}/Cr; Co^{+2}/Co
4	Zn^{+2}/Zn; Bi^{+3}/Bi	13	Mg^{+2}/Mg; Fe^{+2}/Fe
5	Ni^{+2}/Ni; Cr^{+3}/Cr	14	Ag^{+}/Ag; Al^{+3}/Al
6	Cu^{+2}/Cu; Mn^{+2}/Mn	15	Mn^{+2}/Mn; Sn^{+2}/Sn
7	Co^{+2}/Co; Be^{+2}/Be	16	Ni^{+2}/Ni; Cu^{+2}/Cu
8	Pb^{+2}/Pb; Mg^{+2}/Mg	17	Zn^{+2}/Zn; Sn^{+2}/Sn
9	Ti^{+2}/Ti; Sn^{+2}/Sn	18	Zn^{+2}/Zn; Ni^{+2}/Ni

2.4.2. What electrodes may be used for electrolytic production of gas? Make a scheme of electrolysis (anodic, cathodic, net reaction) and determine parameters of electrolysis for your variant in the Table 2.4).

Table 2.4 − Variant of problem

variant	Gas	volume, $м^3$	Electrolyte	Current, A	Time of electrolysis, hour	Current efficiency, %
1	O_2	3,0	NaOH	5000	?	100
2	H_2	4,1	Na_2SO_4	2000	5,0	?
3	Cl_2	?	NaCl	10000	2,0	90
4	O_2	6,7	KNO_3	?	8,0	100
5	H_2	?	LiOH	3000	10,0	100
6	Cl_2	7,0	$BaCl_2$	8000	?	95
7	O_2	?	?	9000	7,5	100
8	H_2	8,8	?	?	3,5	100
9	Cl_2	6,0	?	4000	4,0	?
10	H_2	8,0	Na_2SO_4	?	2	100
11	Cl_2	10,0	KCl	5000	?	94
12	O_2	?	$MgSO_4$	3500	2,5	100
13	Cl_2	5,2	$CaCl_2$	7000	?	97
14	O_2	12,4	?	?	4	100
15	H_2	?	KOH	4200	5	100
16	O_2	?	Rb_2SO_4	1000	1,5	100
17	H_2	7,3	?	?	3	100
18	Cl_2	3,8	NaCl	2220	4	?

2.4.3. Chose the electrolyte and anodic metal for metal coating formation (Table. 2.5). What are the electrolysis reactions? Calculate the electrolysis parameters.

Table 2.5 − Variant of problem

variant	Metal of coating	Metal density ρ, g/cm^3	Coating thickness δ, μm	Current density *j*, A/dm^2	Time of electrolysis, min	Current efficiency, %
1	Ni	8,90	?	1,5	20	90
2	Cd	8,64	7	?	18	98
3	Sn	7,30	9	2,0	10	?
4	Fe	7,87	15	20,0	?	78
5	Cr	7,19	?	8,0	20	30
6	Cu	8,96	3	?	9	100
7	Zn	7,13	12	2,5	21	?
8	Ag	10,50	?	0,8	3	100
9	Au	19,40	1	?	10	100
10	Cd	8,64	6	1,8	?	95
11	Fe	7,87	?	25,0	15	78
12	Cr	7,19	3	6,0	10	?
13	Cu	8,96	5	1,0	?	100
14	Co	8,84	4	?	15	97
15	Zn	7,13	?	1,8	27	87
16	Sn	7,30	8	1,5	?	98
17	Ni	8,90	6	2,5	12	?
18	Ag	10,50	2	1,0	?	100

2.5 EXPERIMENTAL PART

Experiment 1. Electrolysis aqueous solution of $CuSO_4$ with a soluble anode

The process of electrolysis of $CuSO_4$ passing scheme

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

$$\text{Cathode: } Cu^{2+} + 2e = Cu.$$

Electrolyte of composition, g/l: 150 $CuSO_4 \cdot 5H_2O$, 150 H_2SO_4 is used for electrolysis. Adding sulfuric acid explain two reasons: Firstly, it prevents hydrolysis of copper (II) sulfate and, secondly, increases the electrical conductivity of the solution. However, increasing the acid content of more than 200 g/l leads not only to increasing conductivity, but at the same time reduces the solubility of $CuSO_4$. For high *current efficiency* copper conduct process recommended in the absence of oxidants in solution (primarily oxygen of air), causing the side process.

Electrolysis is carried out in the chemical glass with volume of 250–500 ml. Copper samples are used as coaxial anodes with surface 5 times larger than cathode ones. Working voltage is 10–12 V. Current is determined based on surface area *S* and the cathode current density *i* which depends on the composition of the electrolyte and is in this case is 200–300 A/m^2: $I = i \cdot S$. Current is regulated by a rheostat that plug into electrical circuit in series.

The operating procedure:

1. Treat electrodes with sandpaper and wash them thoroughly in distilled water, consider cathode on technical scale.

2. Fill the electrolytic cell with electrolyte solution and dip electrodes in solution.

3. Assemble an electrical circuit according to the Fig. 2.16.

4. Determine the cathode area, and calculate the current.

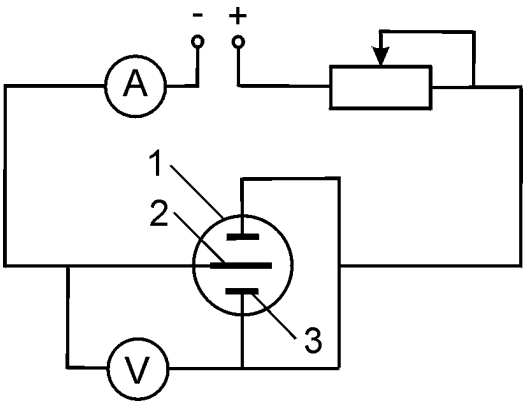


Figure 2.16 – Electrical circuit for electrolysis:
1 – electrolytic cell,
2 – cathode,
3 – anodes

5. Turn the DC source (power source) and adjust rheostat using previously calculated current.

6. Electrolysis is conducted for a time recommended by the teacher. During this time, observe changes occurring (or not occurring) in the electrochemical system.

7. After the process rinse electrodes thoroughly in the water, dry the cathode and consider it again at technical weighing scales. What happens with the mass of the cathode? Explain the results of the experiment.

Experiment 2. Electrolysis of water solution with the gas evolution

The experiment is conducted in a special electrolytic cell for gases producing (Fig. 2.17).

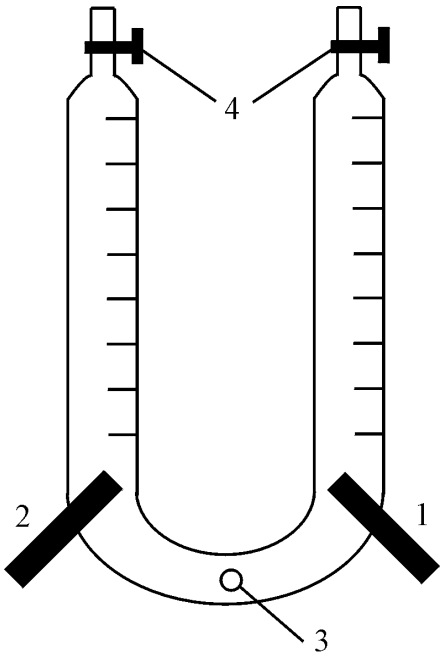


Figure 2.17 – Electrolytic cell for gases receiving:
1, 2 – stainless steel electrodes,
3 – tube accession funnel,
4 – valves

As the electrolyte used is an alkali solution or aqueous solution of any salt which cation and anion are not directly involved in the electrode process. The electrolyte under these conditions only provides electrical conductivity of the solution, and with this in mind, it can supply the following requirements: non-toxic, non-aggressiveness to the electrodes and the electrolytic cell and low cost. This experiment is performed in an electrolyte solution with mass fraction of Na_2SO_4 5 %, which meets the requirements. Following reactions occur at the electrodes:

Anode: $H_2O - 2e = 1 / 2O_2 + 2H^+$

Cathode: $2H_2O + 2e = H_2 + 2OH^-$.

As seen from these equations, the number (and accordingly the volume) of gas released at the cathode, twice the amount of gas released at the anode. Therefore, even though the circuit connection electrolytic cell, you can specify the cathode and anode, based on the volume of gas generated during electrolysis. Can you suggest another way to determine the cathode and anode chemical methods if known reactions that occur on the respective electrodes?

The operating procedure

Fill the electrolytic cell with working solution so that completely to remove air from it. For this purpose solution pours through a funnel with open valves. After the displacement of air valves close and gear check for leaks. For this funnel drop below the level of solution in the electrolytic cell. If the change in position of the solution is not observed, the unit considered sealed.

Assemble the electric circuit scheme Fig. 2.16. Turn on the direct current source and install using rheostat highest possible current. Fix the start of electrolysis. Electrolysis stop after the amount of hydrogen will be equal to 10 ml. Fix the time spent on the electrolysis process, temperature and environment pressure. Based both on the time and current of the electrolysis calculate the theoretical volume of hydrogen V_T, which would evaluate under these conditions.

Having V_T, define the current efficiency for process using the equation Ce = V_E/V_T. Make a conclusion about the process effectiveness basing on the Ce value.

Experiment 3. Study of impurities surfactants for quality metallic coatings

Since electrolytes based on simple salts obtained coarse-grained, dull, rough metal surface. For brilliant, uniform thickness, fine-grained coating deposition shine-form impurities must be added to electrolyte. It can be glycerin, sugar, alcohol or technical surfactants B-7211, LTU, limeda L-2A.

The operating procedure

Fill this electrolytic cell with electrolyte of composition, g/l: $CuSO_4 \cdot 5H_2O$ – 180–240; H_2SO_4 – 45–65; NaCl – 0,05–0,15; additive L-2A – 4–6. Cathode current density varies in the interval of 0.8–1 A/dm^2, temperature of 20 °C, anodes made of pure copper.

Treat electrodes by sandpaper, rinse thoroughly in distilled water and soak in the electrolyte solution. Assemble the electric circuit scheme (Fig. 2.16). Determine the cathode area and calculate operating current. Turn on the DC source and adjust rheostat using previously calculated current.

Electrolysis is conducted for a time that is recommended teacher. After completion of the process electrodes are thoroughly washed with water. Dry and visually assess the quality of the coating.

Experiment 4. Study the sequence of cathodic metal deposition

Predict and then experimentally determine which metal is deposited on a graphite cathode if the electrolysis performed in an electrolyte containing $CuSO_4$ and $FeSO_4$ in equal concentrations. Experiment carried out according to the procedure of the experiment 1. Do the same experimental data with your forecast?

Instability Constants for ions

Complex ion	$K_{нест}$	Complex ion	$K_{нест}$
Ligand NH_3		Ligand I^-	
$[Ag(NH_3)_2]^+$	$9{,}31\ 10^{-8}$	$[CdI_4]^{2-}$	$8{,}00\ 10^{-7}$
$[Co(NH_3)_6]^{3+}$	$1{,}85\ 10^{-6}$	$[HgI_4]^{2-}$	$2{,}53\ 10^{-28}$
$[Cu(NH_3)_4]^{2+}$	$2{,}14\ 10^{-13}$	$[PbI_4]^{2-}$	$1{,}42\ 10^{-4}$
$[Ni(NH_3)_4]^{2+}$	$1{,}12\ 10^{-8}$	$[ZnI_4]^{2-}$	3,22
$[Zn(NH_3)_4]^{2+}$	$3{,}46\ 10^{-10}$	Ligand Br^-	
Ligand OH^-		$[AgBr_2]^-$	$7{,}84\ 10^{-8}$
$[Ag(OH)_2]^-$	$1{,}02\ 10^{-4}$	$[AuBr_2]^-$	$3{,}47\ 10^{-13}$
$[Al(OH)_4]^-$	$3{,}12\ 10^{-33}$	$[CdBr_4]^{2-}$	$2{,}00\ 10^{-4}$
$[Cu(OH)_4]^{2-}$	$2{,}75\ 10^{-15}$	$[HgBr_2]^{2-}$	$1{,}00\ 10^{-21}$
$[Fe(OH)_4]^{2-}$	$2{,}80\ 10^{-9}$	$[PtBr_4]^{2-}$	$3{,}33\ 10^{-21}$
Ligand Cl^-		Ligand OH^-	
$[AgCl_2]^-$	$1{,}76\ 10^{-5}$	$[Ga(OH)_6]^{3-}$	$5{,}00\ 10^{-41}$
$[AuCl_2]^-$	$1{,}61\ 10^{-12}$	$[Pb(OH)_3]^-$	$1{,}20\ 10^{-14}$
$[AuCl_4]^-$	$5{,}00\ 10^{-22}$	$[Sn(OH)_3]^-$	$1{,}18\ 10^{-12}$
$[BiCl_6]^{3-}$	$1{,}70\ 10^{-4}$	$[Zn(OH)_4]^{2-}$	$2{,}32\ 10^{-17}$
$[CdCl_4]^{2-}$	$2{,}30\ 10^{-3}$	Ligand CN^-	
$[CuCl_2]^-$	$3{,}14\ 10^{-6}$	$[Ag(CN)_2]^-$	$8{,}08\ 10^{-22}$
$[HgCl_4]^{2-}$	$8{,}50\ 10^{-16}$	$[Au(CN)_2]^-$	$5{,}00\ 10^{-39}$
$[PdCl_4]^{2-}$	$6{,}02\ 10^{-14}$	$[Au(CN)_4]^-$	$5{,}00\ 10^{-39}$
Ligand I^-		$[Cd(CN)_4]^{2-}$	$1{,}49\ 10^{-19}$
$[AgI_2]^-$	$1{,}81\ 10^{-12}$	$[Fe(CN)_6]^{4-}$	$1{,}00\ 10^{-24}$
$[AgI_3]^{2-}$	$2{,}08\ 10^{-14}$	$[Fe(CN)_6]^{3-}$	$1{,}00\ 10^{-31}$
$[BiI_4]^-$	$1{,}12\ 10^{-15}$	$[Hg(CN)_4]^{2-}$	$4{,}33\ 10^{-42}$

CHAPTER 3 CHEMICAL PROPERTIES OF METALS

3.1 BASIC CONCEPTS AND DEFINITIONS

The vast majority of all elements of the periodic system are metals. From a physical point of view metals are characterized by high thermal and electrical conductivity, mechanical strength, ductility. From a chemical point of view metallic properties of elements are identical to their reducing properties, i.e. in chemical reactions metals act as a reducing agent, and themselves oxidizing (lose electrons):

$$M - ze \rightarrow M^{z+}.$$

The ability of element to lose electrons quantitatively is characterized by E_I ionization potential, the value of which depends on location of the element in the periodic system of elements (PS) (Fig.3.1).

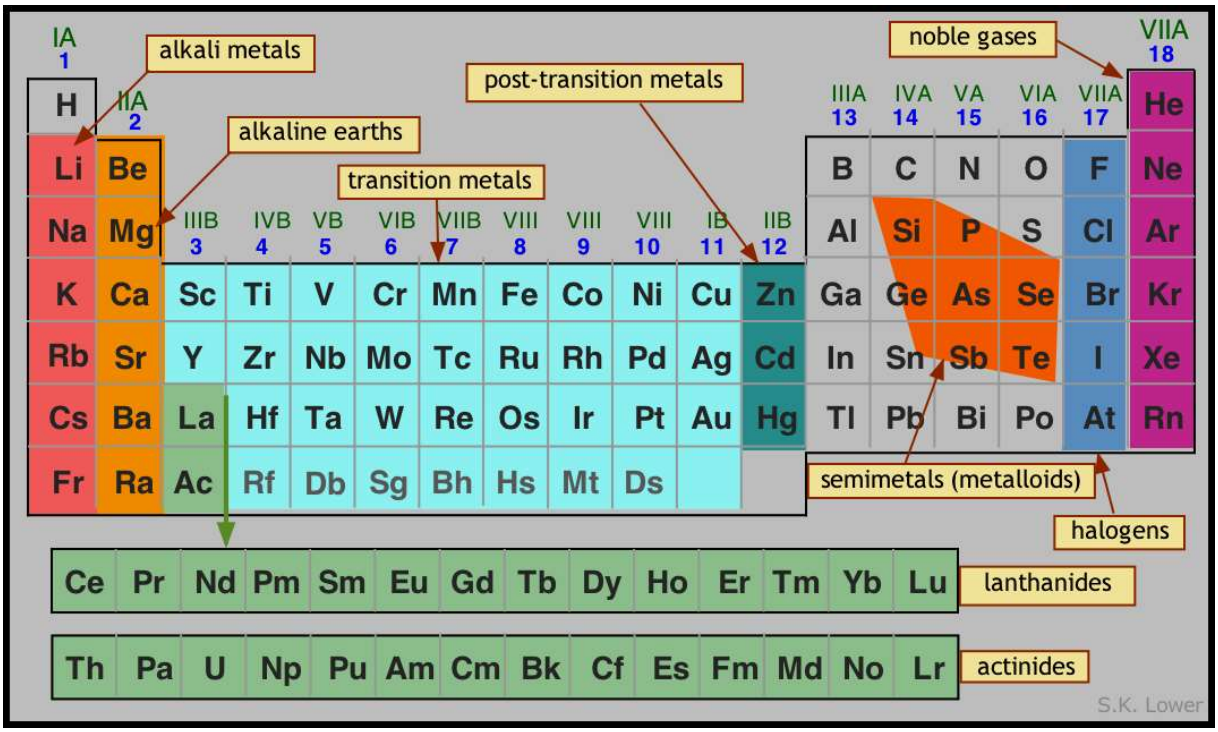


Figure 3.1. Periodic system of elements

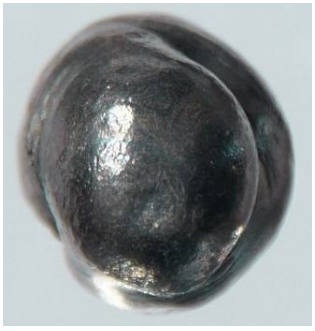
Because in environmental conditions metals are mostly in contact with aqueous solutions or atmosphere that contains water vapor, their chemical activity is correctly to be estimated by the standard electrode potentials. Reactions of metals with components of the environment are redox, therefore, to analyze their probabilities the condition of unauthorized flow should be used, according to which the electrode oxidant potential E_{ox} should be greater than reducing potential E_{red}.

Table 3.1 – Standard electrode potential range (SEPR)

metal	E^0, V	metal	E^0, V	metal	E^0, V	metal	E^0, V
Li^+/Li	–3,045	Al^{3+}/Al	–1,663	Co^{2+}/Co	–0,277	Tc^{2+}/Tc	0,400
Rb^+/Rb	–2,925	Zr^{4+}/Zr	–1,529	Ni^{2+}/Ni	–0,250	Co^{3+}/Co	0,400
K^+/K	–2,924	Ti^{2+}/Ti	–1,210	In^+/In	–0,250	Ru^{2+}/Ru	0,450
Cs^+/Cs	–2,923	V^{2+}/V	–1,186	Mo^{3+}/Mo	–0,200	Cu^+/Cu	0,521
Ba^{2+}/Ba	–2,905	Mn^{2+}/Mn	–1,179	W^{3+}/W	–0,150	Rh^{2+}/Rh	0,600
Sr^{2+}/Sr	–2, 888	Ta^{3+}/Ta	–1,126	Sn^{2+}/Sn	–0,139	Os^{2+}/Os	0,700
Ca^{2+}/Ca	–2, 866	Nb^{3+}/Nb	–1,100	Pb^{2+}/Pb	–0,126	Tl^{3+}/Tl	0,710
Na^+/Na	–2,714	Cr^{2+}/Cr	–0,912	Fe^{3+}/Fe	–0,037	$Hg_2^{2+}/2Hg$	0,789
Ac^{3+}/Ac	–2,600	V^{3+}/V	–0,835	$2H^+/H_2$	0,000	Ag^+/Ag	0,789
La^{3+}/La	–2,522	Zn^{2+}/Zn	–0,763	Ge^{2+}/Ge	0,000	Pb^{4+}/Pb	0,800
Nd^{3+}/Nd	–2,431	Cr^{3+}/Cr	–0,744	Sn^{4+}/Sn	0,009	Hg^{2+}/Hg	0,854
Y^{3+}/Y	–2,372	Ga^{3+}/Ga	–0,529	Bi^{3+}/Bi	0,215	Pd^{2+}/Pd	0,987
Mg^{2+}/Mg	–2, 363	Fe^{2+}/Fe	–0,440	Sb^{3+}/Sb	0,240	Ir^{2+}/Ir	1,100
Sc^{3+}/Sc	–2,077	Cd^{2+}/Cd	–0,403	As^{3+}/As	0,300	Pt^{2+}/Pt	1,188
Be^{2+}/Be	–1, 847	In^{3+}/In	–0,343	Re^{3+}/Re	0,300	Au^{3+}/Au	1,498
Hf^{4+}/Hf	–1,700	Tl^+/Tl	–0,336	Cu^{2+}/Cu	0,340	Au^+/Au	1,692

3.2 METALS OF MAIN SUBGROUPS

3.2.1. *Alkali metals*. The alkali metals are the elements present in the first group of the periodic table (ns^1). They are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs) and Francium (Fr). They are all very reactive metals therefore none of these metals do not occur as free metals in nature. We should store these metals always in inert liquids such as kerosene because they rapidly react with the air, water vapor and oxygen in the air (Fig.3.2). Sometimes they explosively react with other substances. They can achieve the noble gas state easily, by removing the outermost electron in the valence shell. The densities of Lithium and Sodium are less than the density of water. However, the other elements are denser than water.



Be

Mg

Ca

Ba

Figure 3.2. Alkali and alkaline-earth metals

Alkaline earth metals are in the second group of the periodic table (ns^2). Group II elements include; Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra) (Fig.3.3).

Similar to alkaline metals, these elements also do not occur freely in nature and they are also very reactive. They are higher melting and boiling and denser than alkali metals (Table 3.2).

All the elements in this group are denser than water. Pure metals have a silver-grey color, but they tend to decolorize quickly when exposed to air because they form an oxide layer on the surface. Same as alkali metals, these metals are also good conductors in heat and electricity. All of these metals are commercially valuable.

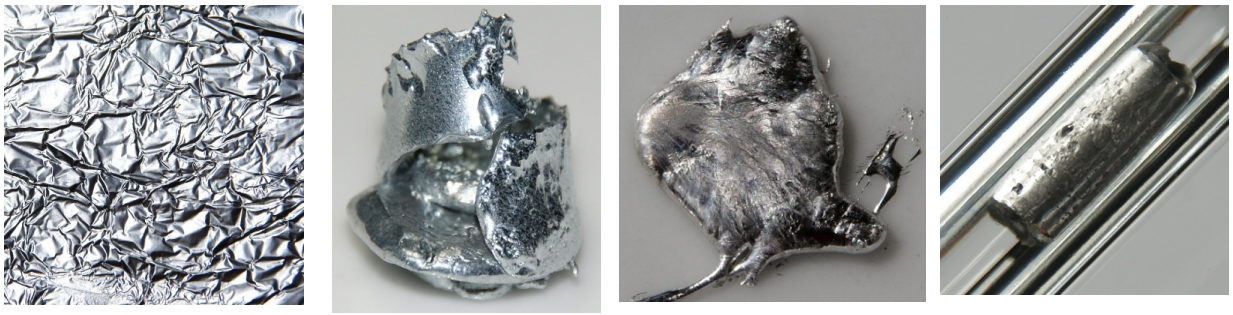
Table 3.2 – Properties of s^2 metals

Property	Be	Mg	Ca	Sr	Ba
Melting point, °C	1283	649	850	770	710
Boiling point, °C	2,970	1,120	1,487	1,367	1,637
Density, g/cm^3	1.86	1.74	1.54	2.67	3.61
Electronegativity (Pauling scale)	1.5	1.2	1.0	1.0	0.9

Alkaline earth metals form OH^- ions when added to water. The solutions of alkaline compounds have higher pH values (>7). These alkaline compounds also can turn red color litmus into blue. They have basic properties. Alkaline earth metals are harder than alkali metals. These elements form +2 cations because they have two valence electrons and, a cation can be formed by removing those electrons. However, since these electrons are in the s orbital as an electron pair, these elements are not that much reactive.

Metals of III A group (Fig.3.3) are in the third group of the periodic table (ns^2np^1), the stable oxidation # is +3 except Thallium which stable oxidation # is +1. Aluminum is the third most abundant element in the earth's crust. It is just slightly less reactive than the active metals. The other three elements in this group are active metals, but they are so scarce they are of limited interest. Gallium, Indium, and Thallium combined total less than 10^{-10}% of the earth's crust. Aluminum, Gallium,

Indium are amphoteric metals, and properties of Thallium close to the alkaline-earth metals.



Al Ga In Tl

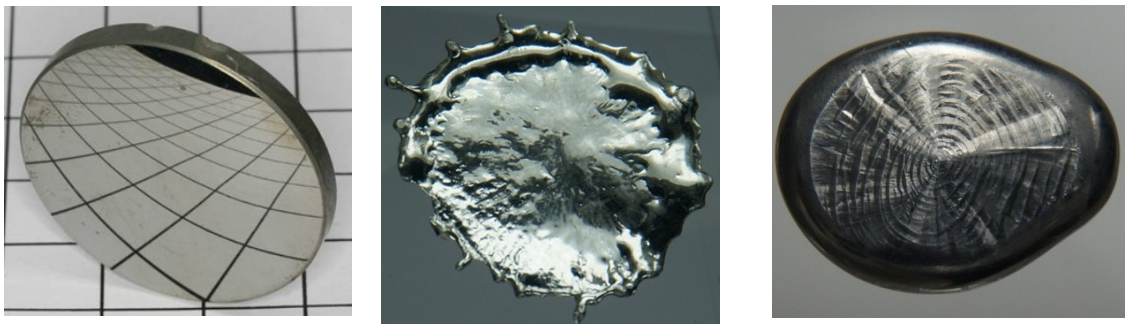
Figure 3.3. Metals of IIIA group

The physical properties of the metals are given in the Table 3.3.

Table 3.3 – Properties of s^2p^1 metals

Property	Aluminum	Gallium	Indium	Thallium
Melting point, °C	660	30	157	304
Boiling point, °C	2,519	2,204	2,072	1,473
Density, g/cm^3	2.7	5.9	7.3	11.85
Electronegativity (Pauling scale)	1.6	1.8	1.7	1.6

The metals in Group IVA – germanium Ge, tin Sn, lead Pb has electronic structure of valence level ns^2np^2 (Fig.3.4).



Ge Sn Pb

Figure 3.4. Metals of IVA group

Lead is a true metal, tin is almost completely metallic; germanium is metallic in appearance and in a number of its other physical properties, but the properties of many of its compounds are those of derivatives of nonmetals. The stable oxidation # for lead is +2, but in some substances (PbO_2) which exhibit oxidizing properties Pb is +4; the stable oxidation # for germanium and tin is +4, but Sn^{2+} substances are also widely known.

The physical properties of the metals are given in the Table 3.4.

Table 3.4 – Properties of s^2p^2 metals

Property	Germanium	Tin	Lead
Melting point, °C	938	232	328
Boiling point, °C	2,833	2,602	1,749
Density, g/cm^3	2.7	5.9	7.3
Mohs Hardness	6.0	1.5	1.5
Electronegativity (Pauling scale)	1.8	1.8	1.9

In V A group (ns^2np^3) there are two metalloids – Arsenic and Antimony with stable oxidation # +5 (and +3 in some substances As_2S_3, Sb_2S_3 etc.), and a metal Bismuth of stable oxidation # +3 (and +5 in some substances $KBiO_3$) (Fig.3.5).

As Sb Bi

Figure 3.5. Metals of VA group

Arsenic exists in the form of two allotropic modifications: metallic arsenic, which is a stable metallic look like solid, and yellow arsenic

which is not stable. Metallic arsenic sublimates at heating up. Antimony has two allotropies also. One is crystalline metallic look like solid, it's very brittle. Yellow allotropy of antimony is unstable like that of arsenic. Bismuth is a glittery reddish-white metal. It's brittle solid and a currency conductor.

The physical properties of the metals are given in the Table 3.5.

Table 3.5 – Properties of s^2p^3 metals

Property	Germanium	Tin	Lead
Melting point, °C	817	630	271
Boiling point, °C	631	1,750	1,560
Density, g/cm^3	5.7	6.7	9.8
Electronegativity (Pauling scale)	2.0	1.9	1.9

3.3 TRANSITION METALS

3.3.1. Metals of VIIIB group (Fig.3.6). Metals of *Iron family* have electronic configuration $3d^{6\text{-}8}4s^2$, thus their oxidation state depends on the nature of oxidizing agent. These metals are rather active according to standard potentials (Table 3.1).

Fe Co Ni

Figure 3.6. Metals of VIIIB group

The physical properties of the metals are given in the Table 3.6.

Table 3.6 – Properties of iron family metals

Property	Iron (Fe)	Cobalt (Co)	Nickel (Ni)
Melting point, °C	1,538	1,495	1,455
Boiling point, °C	2,862	2,870	2,927
Density, g/cm^3	7.87	8.9	8.9
Mohs Hardness	4.0	5.0	4.0
Electronegativity (Pauling scale)	1.8	1.9	1.9
Oxidation state	6, **3**, 2, 0	4, **3**, **2**, 0	3, **2**, 0

Palladium and Platinum family metals (Fig.3.7) have configuration $4d^{6\text{-}8}5s^2$ and $5d^{6\text{-}8}6s^2$ respectively. The chemical activity of these metals differs significantly from the metals of the iron family. The mentioned metals are among low-active and noble ones, as follows from their standard potentials (Table 3.1). A number of oxidation states for above metals is wider as compared with Iron family due to appearance of empty 4f orbital.

Ru Rh Pd Os Ir Pt

Figure 3.7. Metals of VIIIB group

The physical properties of the metals (Table 3.7) differ from iron family by higher melting and boiling point and density. Palladium and Platinum family metals are known as high-density refractory ones. It should also be noted their outstanding catalytic activity in many redox reactions and technological processes.

Table 3.7 – Properties of iron family metals

Property	Ru	Rh	Pd	Os	Ir	Pt
Melting point, °C	2,334	1,964	1,555	3,033	2,446	1,768
Boiling point, °C	4,150	3,695	2,963	5,012	4,130	3,825
Density, g/cm^3	12.45	12.4	12.0	22.6	22.56	21.45
Mohs Hardness	6.5	6.0	4.75	7.0	6.5	3.5
Electronegativity (Pauling scale)	2.2	2.28	2.2	2.2	2.2	2.28
Oxidation state	+2 – +8, **+3**, **+4**	+2 – +6, **+3**	0 – +4, **+2**, **+4**	0 – +8, **+4**	0 – +9, **+3**, **+4**	0 – +6, **+4**

3.3.2. Metals of IB group have electronic configuration (n–1)d^{9}ns^2, but there is a their oxidation state depends on the nature of oxidizing agent. These metals are low active according to standard potentials (Table 3.1) and electronegativity (Table 3.8).

Copper (Cu) is a soft, malleable, and ductile metal with very high thermal and electrical conductivity of pinkish-orange color (Fig.3.8). Copper is used as a conductor of heat and electricity, as a building material, and as a base of various metal alloys. *Silver* (Ag) is a soft, white, lustrous transition metal, it exhibits the highest electrical conductivity, thermal conductivity, and reflectivity of any metal.

Copper Cu

Silver Ag

Gold Au

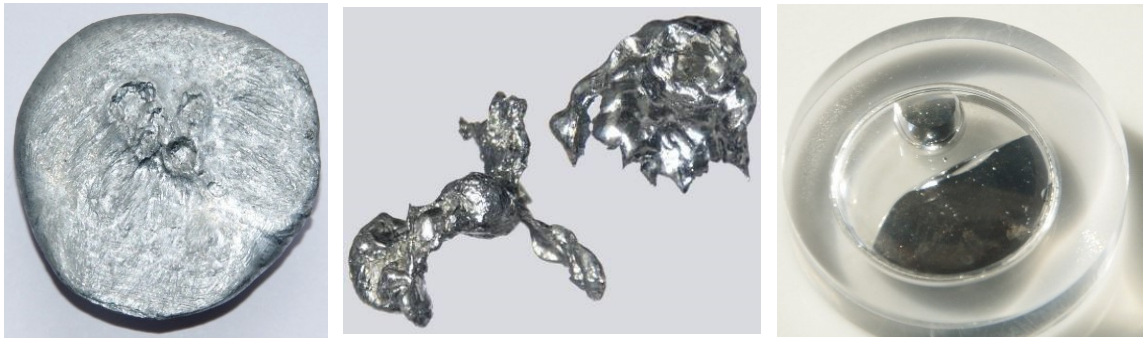
Figure 3.8. Metals of IB group

The physical properties of the metals are given in the Table 3.8.

Table 3.8 – Properties of IB group metals

Property	Cu	Ag	Au
Melting point, °C	1,085	962	1,064
Boiling point, °C	2,562	2,162	2,970
Density, g/cm^3	8.96	10.49	19.3
Mohs Hardness	3.0	2.5	2.5
Electronegativity (Pauling scale)	1.9	1.92	2.54
Oxidation state	+1, **+2**, +3	**+1**, +2, +3	**+1**, +2, **+3**

3.3.3. Metals of IIB group (Fig.3.9) Zinc Zn, Cadmium Cd, Mercury Hg have electronic configuration $(n–1)d^{10}ns^2$, and their oxidation state commonly is +2, excepting Mercury which oxidation # may be +1 due to formation Hg–Hg bonds. The chemical properties of above metals also differ significantly. Zinc is a moderately active amphoteric metal and strong reducing agent. Cadmium is a soft, malleable, ductile, bluish-white divalent metal. It exhibits basic behavior and forms complex compounds. Unlike most other metals, cadmium is resistant to corrosion. Mercury is a heavy, silvery-white low reactive liquid metal. Compared to other metals, it is a poor conductor of heat, but a fair conductor of electricity.



Zn Cd Hg

Figure 3.9. Metals of IIB group

The physical properties of the metals are given in the Table 3.9.

Table 3.9 – Properties of IIB group metals

Property	Zn	Cd	Hg
Melting point, °C	420	321	–39
Boiling point, °C	907	767	357
Density, g/cm^3	7.14	8.65	13.534
Mohs Hardness	2.5	2.0	–
Electronegativity (Pauling scale)	1.65	1.69	2.0
Oxidation state	+2	+2	+1, **+2**

3.3.4. Metals of IIIB group (Scandium Sc, Yttrium Y, Lanthanum La) are rare-earth metals similar in chemical properties to the Aluminum family namely they are trivalent amphoteric. The configuration of valence sublevels (n–1)d^{1}ns^2 as well as standard potentials confirm their high reactivity.

3.3.5. Metals of IVB (n–1)d^{2}ns^2 (Titanium Ti, Zirconium Zr, Hafnium Hf) and VB (n–1)d^{3}ns^2 groups (Vanadium V, Niobium Nb, Tantalum Ta) are widely known as valve metals due to formation acidic semi conductive or insulator oxides (Fig.3.10). Atmospheric passivation gives above metals excellent resistance to corrosion, almost equivalent to platinum.

Ti Zr Hf V Nb Ta

Figure 3.10. Valve metals

Titanium is used in steel as an alloying element (ferro-titanium) to reduce grain size and as a deoxidizer, and in stainless steel to reduce carbon content. Zirconium is mainly used as a refractory and opacifier, although small amounts are used as an alloying agent for its strong resistance to corrosion. The physical properties of the metals are given in the Table 3.10.

Table 3.10 – Properties of VIB group metals

Property	Ti	Zr	Hf	V	Nb	Ta
Melting point, °C	1,668	1,855	2,233	1,910	2,477	3,017
Boiling point, °C	3,287	4,377	4,603	3,407	4,744	5,458
Density, g/cm^3	4.5	6.52	13.31	6.0	8.57	16.7
Mohs Hardness	6.0	5.0	5.5	6.7	6.0	6.5
Electronegativity (Pauling scale)	1.54	1.33	1.3	1.63	1.6	1.5
Oxidation state	0 – +4, **+4**	0 – +4, **+4**	0 – +4, **+4**	0 – +5, **+5**	0 – +5, **+5**	0 – +5, **+5**

Vanadium family metals have good resistance to corrosion and they are stable against alkalis and sulfuric and hydrochloric acids. Above metals are medium-hard, ductile, steel-blue or lustrous grey, electrically conductive and thermally insulating ones.

3.3.6. Metals of VIB group $(n–1)d^4ns^2$ (Fig.3.11) Chromium Cr, Molybdenum Mo, Tungsten W differ both by physical properties (Table. 3.11) and chemical reactivity as follows from standard potentials (Table. 3.1). Chromium has an electron configuration of $[Ar]3d^54s^1$, owing to the lower energy of the high spin configuration. Chromium exhibits a wide range of oxidation states, but most stable ionic state is +3. The oxidation states +3 and +6 occur the most commonly. Chromium metal has negative potential (left standing), but in air it is passivated by oxidation, forming a thin (only a few molecules thick), protective, surface layer. That

causes rather high corrosion resistance in atmosphere. Chromium also is positioned as hard metal (Table 3.11) that expands its industrial scope.

Cr Mo W

Figure 3.11. Metals of VIB group

The physical properties of the metals are given in the Table 3.11.

Table 3.11 – Properties of VIIB group metals

Property	Cr	Mo	W
Melting point, °C	1,907	2,623	3,422
Boiling point, °C	2,671	4,639	5,930
Density, g/cm^3	7.19	10.28	19.3
Mohs Hardness	8.5	5.5	7.5
Electronegativity (Pauling scale)	1.66	2.16	2.36
Oxidation state	0 – +6, **+3**, **+6**	0 – +6, **+4**, **+6**	0 – +6, **+4**, **+6**

Molybdenum does not visibly react with oxygen or water at room temperature. Weak oxidation of molybdenum starts at 300 °C; bulk oxidation occurs at temperatures above 600 °C, resulting in molybdenum trioxide. Like many heavier transition metals, molybdenum shows little inclination to form a cation in aqueous solution, although the Mo^{3+} cation is known under carefully controlled conditions. In its raw form, tungsten is a hard steel-grey metal that is often brittle and hard to work. Elemental tungsten resists attack by oxygen, acids, and alkalis. The most common formal oxidation state of tungsten is +6, but it exhibits all oxidation states

from 0 to +6. Tungsten typically combines with oxygen to form the yellow tungstic oxide, WO_3, which dissolves in aqueous alkaline solutions to form tungstate ions, WO_4^{2-}.

3.3.7. Metals of VIIB group $(n-1)d^5ns^2$ (Fig.3.12) are Manganese Mn, Technetium Tc, Rhenium Re. The chemical properties of above metals also differ significantly. Manganese is a silvery-gray metal that resembles iron. It is hard and very brittle, difficult to fuse, but easy to oxidize. Manganese is a metal with important industrial metal alloy uses, particularly in stainless steels. Its chemical properties are similar to iron. Technetium is a radioactive metal, the most stable isotope is the fully ionized ^{97}Tc. Technetium is located in the seventh group of the periodic table, between rhenium and manganese. As predicted by the periodic law, its chemical properties are between those two elements. Of the two, technetium more closely resembles rhenium, particularly in its chemical inertness and tendency to form covalent bonds.[26] Unlike manganese, technetium does not readily form cations (ions with a net positive charge).

Mn Tc Re

Figure 3.12. Metals of VIIIB group

Technetium exhibits nine oxidation states from −1 to +7, with +4, +5, and +7 being the most common. Technetium dissolves in aqua regia, nitric acid, and concentrated sulfuric acid, but it is not soluble in hydrochloric acid of any concentration. Metallic technetium slowly tarnishes in moist air and, in powder form, burns in oxygen.

Rhenium is a silvery-white metal with one of the highest melting points of all elements, exceeded by only tungsten and carbon. It also has one of the highest boiling points of all elements. It is also one of the densest, exceeded only by platinum, iridium and osmium. Its usual commercial form is a powder, but this element can be consolidated by pressing and sintering in a vacuum or hydrogen atmosphere. When annealed this metal is very ductile and can be bent, coiled, or rolled. Rhenium-molybdenum alloys are superconductive at 10 K; tungsten-rhenium alloys are also superconductive around 4–8 K, depending on the alloy. Rhenium metal is a superconductor at 1.697±0.006 K.

In bulk form and at room temperature and atmospheric pressure, the element resists alkalis, sulfuric acid, hydrochloric acid, dilute (but not concentrated) nitric acid, and aqua regia.

The physical properties of the metals are given in the Table 3.12.

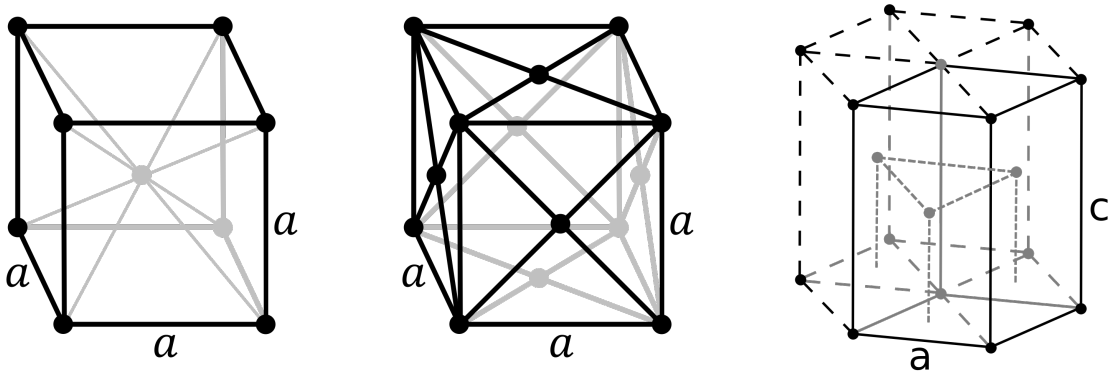
Table 3.12 – Properties of VIIB group metals

Property	Mn	Tc	Re
Melting point, °C	1,246	2,157	3,186
Boiling point, °C	2,061	4,265	5,630
Density, g/cm^3	7.21	11	21.02
Mohs Hardness	6.0	–	7.0
Electronegativity (Pauling scale)	1.55	1.9	1.9
Oxidation state	0 – +7 **+2**, **+4**, **+7**	0 – +7, **+4**, **+7**	0 – +7, **+4**

Thus Mo, W, Re, Os, Ir, valve metals are known as refractory ones. Most metals have very compact crystal lattices: cubic body-centered bcc (Fig.3.13 a), cubic face-centered fcc (Fig.3.13 b), hexagonal close-packed hcp (Fig.3.13 c). Every atom in a metal is usually surrounded by 8 or 12 nearest neighbors.

The nature of bonding in metals is provided by their ability to conduct electricity. The freedom of *e* movement is caused by the fact that

the valence electrons are completely delocalized (form an electron gas**)**. Positive metal ions produced by the loss of these valence electrons are held in place by the attraction of the negatively charged electron gas.



a	b	c
Fe, V, Nb, Ta, Cr, Mo, W	Al, Ni, Ag, Cu, Au, Pd, Pt, Sn, Pb	Be, Ti, Zr, Zn, Mg, Co, Cd

Figure 3.13. Cristal lattice of metals

Metals exhibit high electrical and thermal conductivity. Electrical conductivity decreases as the temperature is raised. Exactly the opposite behavior is found for semiconductors: with increasing temperature, more and more electrons are excited to the higher-energy conduction band so that more current can be carried.

While the alkali metals and some of the alkaline-earth metals can be cut with a knife, metals like tungsten are hard enough to scratch the knife itself. A good indication of how the strength of the metallic bonding as well as the other properties such as boiling and melting points, density, and hardness varies with position in the periodic table is given in above tables.

3.4 CHEMICAL PROPERTIES OF METALS

3.4.1. Reactions with simple substances depends on the reactivity of the metal and oxidizing strength of nonmetal. All metals except gold burn in oxygen (Table 3.13).

Table 3.13 – Reactions of metals with oxygen

O_2	Metal	Products
	Alkali alkali-earth	M_2O_2 MO_2
	All metals	M_2O_x
	Noble metals (Au)	–

where x – the oxidation number of a metal.

Metals according to their placement in standard electrode potential raw (SEPR) react with Halogens producing halides of composition $MHal_x$ (Table 3.14).

Table 3.14 – Reactions of metals with oxygen

Halogen	Metal	Products
F_2, Cl_2	All	$MHal_x$
Br_2	up to Ag in SEPR	
I_2	up to Cu in SEPR	

3.4.2. Metals reaction with water obeys the following rules: metal is oxidized by hydrogen ions according the following reactions. Thus, only active metals having potentials lower than 0.5 V are thermodynamically instable in water. But only alkali and alkaline-earth metals dissolve in

water due to solubility of their hydroxides. Other active metals may react with vapor producing appropriative oxides.

$M \rightarrow M^{n+} + ne,$ $E_{M^{n+}/M}$

$2H_2O + 2e \rightarrow H_2 + 2OH^-$ $E_{H_2/H_2O} = -0.059\,pH,$

For neutral medium pH7 $E_{H_2/H_2O} = -0.413$ V

If $E_{M^{n+}/M} < -0.413$ V, and a metal hydroxide is soluble metal will react with water :

$2Na + 2H_2O \rightarrow H_2 + 2NaOH$

If metal hydroxide is unsoluble the reaction occures under heating (with steam) :

$Zn + H_2O \rightarrow H_2 + ZnO$

A range of active metals those electrode potentials are more negative than –0.413 V could not react with water due to the acidic nature of oxide film on their surface which is forming in contact with oxygen or oxygen-containing compounds (Table 3.15).

Table 3.15 – Metals which are passivated on air

Metal	Ti, Zr, Hf	Ta, Nb, V	W, Mo
Acidic oxide	MO_2	M_2O_5	MO_3

3.4.2. Reactions non-oxidizing acids with metals obey the following rules: only metals located before hydrogen in SEPR may reduce hydrogen from acidic medium. Exceptions are metals which form insoluble salts. For example, copper does not dissolve in hydrochloric or dilute sulfuric acid, since its potential is greater than the potential of hydrogen evolution. And nickel reacts with the above mentioned acids. Lead – acid reactions are limited by the low solubility of most salts, in particular chlorides and sulfates.

$$M \rightarrow M^{n+} + ne, \qquad E_{M^{n+}/M}$$

$$2H^+ + 2e \rightarrow H_2 \qquad E_{H_2/H^+} = -0.059\,\text{pH},$$

For acid medium pH0 $E_{H_2/H^+} = 0.0$ V

If $E_{M^{n+}/M} < 0.0$ V, and a metal salt is soluble

metal will react with acid :

$$Ni + 2HCl \rightarrow H_2 + NiCl_2$$

If metal salt is unsoluble the metal becomes passive :

$$Pb + 2HCl \rightarrow H_2 + PbCl_2 \downarrow$$

3.4.3. Reaction with acids – oxidizing agents. Reaction with nitric acid possesses through oxidation of metal by nitrogen (V):

$$M + HNO_3 \rightarrow M(NO_3)_x + A + H_2O$$

1. $NO_3^- + 3e + 4H^+ \rightarrow NO + 2H_2O$, $E^0 = +0.96$;

2. $NO_3^- + e + 2H^+ \rightarrow NO_2 + H_2O$, $E^0 = +0.78$;

3. $NO_3^- + 8e + 10H^+ \rightarrow NH_4^+ + 3H_2O$, $E^0 = +0.87$

The product of N(V) reducing depends both on the activity of metal and concentration of the acid (Table 3.16).

Table 3.16 – Products of nitrogen reduction

The nitrogen reduction products A nature			
Metal	Concentration of acid ω, %		
	Delute ω<15	Middle 15<ω<40	Concentrated ω>45
Active up to Zn	$N^{-3}H_4NO_3$ or NH_3	N_2O, N_2	NO_2
Middle activity from Zn to Pb	N_2 under heating	NO	NO_2 under heating
Inactive from Ge to Au	–	NO	

Reaction with concentrated sulfuric acid possesses through oxidation of metal by sulphur (VI):

$$M + H_2SO_{4(concentrated)} \rightarrow M_2(SO_4)_x + Y + H_2O$$

1. $SO_4^{2-} + 2e + 4H^+ \rightarrow SO_2 + 2H_2O$, $E^0 = +0.48$;
2. $SO_4^{2-} + 6e + 8H^+ \rightarrow S + 4H_2O$, $E^0 = +0.36$;
3. $SO_4^{2-} + 8e + 10H^+ \rightarrow H_2S + 4H_2O$, $E^0 = +0.15$.

The product of S(VI) reducing depends both on the activity of metal and concentration of the acid (Table 3.17).

Table 3.17 – Products of nitrogen reduction

The sulfuric reduction product Y nature			
Metal	Concentration of acid ω, %		
	Delute ω<15	Middle 15<ω<40	Concentrated ω>45
Active up to Zn	H_2	S	H_2S
Middle activity from Zn to Pb			SO_2 under heating
Inactive from Ge to Ag	–	–	

Concentrated acids oxidize metals for higher oxidizing state.

1. $Fe + H_2SO_{4(diluted)} \rightarrow FeSO_4 + H_2$,

   $Fe^0 - 2e \rightarrow Fe^{2+}$; $2H^+ + 2e \rightarrow H_2$
2. $2Fe + 4H_2SO_{4(concentrated)} \xrightarrow{T} Fe_2(SO_4)_3 + S + 4H_2O$,

   $Fe^0 - 3e \rightarrow Fe^{3+}$

   $SO_4^{2-} + 6e + 8H^+ \rightarrow S + 4H_2O$
3. $3Sn + 8HNO_{3(diluted)} \rightarrow 3Sn(NO_3)_2 + 2NO + 4H_2O$

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

   $NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$
4. $Sn + 8HNO_{3(diluted)} \rightarrow SnO_2 + NO_2 + 4H_2O$

   $Sn + 2H_2O - 4e \rightarrow SnO_2 + 4H^+$

   $NO_3^- + 2H^+ + e \rightarrow NO_2 + H_2O$

Noble and semi-noble metals may be dissolved in a mixture of acids containing oxidizing agent and ligand. Oxidizable metal forms a complex with a ligand due to which the potential shifts to the negative side:

$$Au + HNO_3 + 4HCl \rightarrow H[AuCl_4] + NO + 2H_2O,$$

$$Au^0 + 4Cl^- - 3e \rightarrow [AuCl_4]^- \qquad E_{[AuCl_4]^-/Au} = 0.82\ V,$$

$$NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O \qquad E_{NO_3^-/NO} = 0.96\ V,$$

$$Cl^- - ligand;\ NO_3^- - oxidant$$

Passivating metals also may be dissolved in a mixture of acids containing ions – depassivator which destroys protective oxide film on the metal surface:

$$3Ta + 5\,HNO_3 + 21HF \rightarrow\ 3H_2[TaF_7] + 5NO + 10H_2O,$$

$$Ta^0 + 7F^- - 5e \rightarrow\ [TaF_7]^{2-}\ , \qquad F^- - ligand,\ depasivator$$

$$NO_3^- + 4H^+ + 3e \rightarrow\ NO + 2H_2O,\ NO_3^- - oxidant$$

3.4.4. Amphoteric metals (Be, Zn, Al, In, Ga, Sn, Pb) react with alkali solutions according to the Table 3.18.

$$Zn + 2NaOH + 2H_2O \rightarrow Na_2[Zn(OH)_4] + H_2$$

$$Zn^0 + 4OH^- - 2e \rightarrow [Zn(OH)_4]^{2-} \qquad E_{[Zn(OH)_4]^{2-}/Zn} = -1.245\ V,$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^-, \text{if pH14} \qquad E_{H_2/H_2O} = -0.82\ V,$$

Table 3.17 – Potentials of metal / metal hydroxide complexes

Half-reaction	Standard potential, V
$Al + 4OH^- - 3\,e \rightarrow [Al(OH)_4]^-$	–2.350
$Be + 4OH^- - 2\,e \rightarrow [Be(OH)_4]^{2-}$	–2.115
$Zn + 4OH^- - 2\,e \rightarrow [Zn(OH)_4]^{2-}$	–1.245
$Ga + 4OH^- - 3\,e \rightarrow [Ga(OH)_4]^-$	–1.219
$In + 4OH^- - 3\,e \rightarrow [In(OH)_4]^-$	–1.000
$Sn + 4OH^- - 2\,e \rightarrow [Sn(OH)_4]^{2-}$	–0.909
$Pb + 4OH^- - 2\,e \rightarrow [Pb(OH)_4]^{2-}$	–0.872

Transition polyvalent metals react with alkali solutions containing oxidizing agent. The latter converts the metal to the oxidation state, which corresponds to an amphoteric oxide or a hydroxide.

Cr, W, Mn, Fe *etc* are reacted with alkali solutions
in the presence of oxidant (H_2O_2, $KClO_3$, $NaNO_3$ *etc*)

$$2Fe + 2NaOH + 3H_2O_2 \rightarrow 2NaFeO_2 + 4H_2O,$$

$$Fe^0 + 4OH^- - 3e \rightarrow FeO_2^- + 2H_2O,$$

$$H_2O_2 + 2e \rightarrow 2OH^-$$

H_2O_2 – oxidant.

Noble metals react with alkali solutions containing oxidizing agent and ligand. Oxidizable metal forms a complex with a ligand due to which the potential shifts to the negative side:

$$4Au + 2H_2O + O_2 + 8NaCN \rightarrow 4Na[Au(CN)_2] + 4NaOH,$$

$$Au^0 + 2CN^- - e \rightarrow [Au(CN)_2]^-, E_{[Au(CN)_2]^-/Au} = -0.611\ V,$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-, \qquad E_{O_2/OH^-} = 0.413\ V,$$

CN^- – ligand, O_2 – oxidant.

3.4.5. Metal reactions with salts obey the rule: cation of metal with larger standard potential (E^0) is an oxidizing agent for the metal with lower E^0:

$$Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag;$$

$$Ag^+ + e \rightarrow Ag^0,\ E^0(Ag^+/Ag)=0.789\ V;$$

$$Cu^0 - 2e \rightarrow Cu^{2+},\ E^0(Cu^{2+}/Cu)=0.340\ V.$$

However, in solutions of salts, hydrolysis reactions can occur, which significantly change the acidity of the medium. Reactions metals with salts under hydrolysis must consider the possibility of dissolving the metal in acid or alkali. For example, aluminum cannot displace more active sodium from a solution of its salt. At the same time, sodium carbonate will

dissolve aluminum due to alkalization of the medium as a result of hydrolysis.

$$Al + Na_2CO_3 + H_2O \rightarrow ?$$

1. $E^0_{Al^{3+}/Al} = -1.63 > E^0_{Na^+/Na} = -2.73;$

2. Hydrolysis: $Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}$,

$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-;$

3. Reaction in alkali solution :

$Al^0 + 4OH^- - 3e \rightarrow [Al(OH)_4]^-$,

$2H_2O + 2e \rightarrow H_2 + 2OH^-$;

4. Net reaction :

$$2Al + 2Na_2CO_3 + 8H_2O \rightarrow 2Na[Al(OH)_4] + 2NaHCO_3 + 3H_2$$

The other example: iron cannot displace more active aluminum from a solution of its salt. At the same time, aluminum chloride will dissolve iron due to acidification of the medium as a result of hydrolysis:

$$Fe + AlCl_3 + H_2O \rightarrow ?$$

1. $E^0_{Al^{3+}/Al} = -1.63 < E^0_{Fe^{2+}/Fe} = -0.44;$

2. Hydrolysis: $AlCl_3 \rightarrow 3Cl^- + Al^{3+}$,

$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+;$

3. Reaction with acid

$Fe^0 - 2e \rightarrow Fe^{2+}$,

$2H^+ + 2e \rightarrow H_2$;

4. Net reaction :

$$Fe + 2AlCl_3 + 2H_2O \rightarrow FeCl_2 + 2AlOHCl_2 + H_2$$

3.5 CONTROL TASKS

3.5.1. What properties of the metal can be defined based on its position in a row of standard electrode potentials? Make up the equation of chemical reactions that confirm your conclusions on the example of groups of metals according to the options (Table 3.18).

3.5.2. Analyze whether the metal contained in your variant (Table 3.19), interact with water, solutions of HCl and HNO_3 (diluted and

concentrated, in cold and when heated), alkaline solution (NaOH + H_2O), sodium carbonate and aluminum chloride (consider the possibility of hydrolysis of salts) or $AgNO_3$, and provide appropriate equations of chemical reactions.

Table 3.18 – Variants of tasks

variant	Metals	variant	Metals	variant	Metals
1	Li, Zn, Ag	9	Mg, Co, Re	17	Ba, Zn, Sb
2	Na, Cd, Cu	10	Sr, Ni, Cu	18	Ca, Cr, Re
3	Ba, Fe, Hg	11	Ca, Mo, Ru	19	Na, Ga, Cu
4	Ca, Ni, Au	12	Rb, Sn, Rh	20	Sr, Fe, Hg
5	Sr, Mn, Bi	13	Li, Pb, Ag	21	Cs, In, Ag
6	K, Co, Pd	14	Be, W, Os	22	Rb, Mn, Tc
7	Cs, Cd, Sb	15	Mg, Al, Pd	23	Li, Ti, Ru
8	Ba, Tl, Bi	16	K, Mn, Ge	24	Sr, Pb, Ge

Table 3.19 – Variants of tasks

variant	Metals	variant	Metals	variant	Metals
1	Be	9	Cd	17	Mg
2	Cr	10	Sn	18	W
3	Co	11	Mn	19	Nb
4	Cu	12	Al	20	Zr
5	Zn	13	Bi	21	V
6	Fe	14	Ti	22	Mo
7	Ni	15	Sb	23	Ta
8	Pb	16	Ag	24	Pd

3.6 EXPERIMENTAL PART

Experiment 1. Study of the metal's activity in neutral medium

1.1. Pour 2–3 ml of water and add 3–4 drops of phenolphthalein in a test tube. Put a piece of magnesium in a test tube, and then heat the tube. Explain, why the changes in a test tube occur only when it's heated? Make up the equation of occurring reactions.

1.2. Pour 1–2 ml soluble salts of sodium, copper (II), aluminum, zinc in four test tubes and place a piece of magnesium in each of them. Explain why the reaction does not proceed in all of the test tubes? Write the equation of occurring reactions, make an electronic balance, and

indicate oxidizing and reducing agent. Note the gas which is released during certain reactions and explain what this gas is, considering the possibility of salts hydrolysis.

1.3. Dip a piece of aluminum in two test tubes. Pour 1–2 ml of copper (II) chloride in one of them, and into the second – the same volume of copper (II) sulfate solution. Is the rate of reaction in both tubes the same? Conduct the similar experiments using magnesium, beryllium, and titanium. Make a conclusion about the chemical resistance of these metals in the presence of chloride ions. Explain the effect of chloride ions on the chemical behavior of metals.

Experiment 2. The influence of hydrochloric and dilute sulfuric acids on metals

2.1. Pour 1–2 ml of 10% sulfuric acid solution into the three test tubes and put a piece of metal to each of them: in the first – zinc, in the second – iron, in the third – copper. If the reaction is slow, the tube must be heated. Repeat the experiment, replacing sulfuric acid to hydrochloric one. In which cases the reaction occurs? Why? Write the equations of possible reactions. What element is an oxidant for metal in these reactions? Explain the intensity of reactions in terms of metals location in the standard electrode potentials row.

2.2. Investigate the lead behavior in the dilute hydrochloric and sulfuric acids. Does the lead react with these acids? How could this be explained considering its negative potential?

Experiment 3. Effects of concentrated sulfuric acid on metals

3.1. Pour 1–2 ml of concentrated sulfuric acid in two test tubes and place in them: into the first – a piece of magnesium, into the second – a piece of copper. Write the reactions, considering that the ion-oxidizer SO_4^{2-} reduces in the first case to H_2S, in the second – to SO_2.

3.2. Add two pieces of lead into two test tubes. Pour concentrated hydrochloric acid into the first tube, and concentrated sulfuric acid into the

second. Explain reactions of lead with sulfuric and hydrochloric acids of different concentrations (see experiment 2.1).

3.3. Place two pieces of iron into the two test tubes, pour the diluted sulfuric acid into one of them, and concentrated into the second. Heat up the tubes. Add 1–2 drops of hexacyanoferrate (III) (K_3 [Fe ($CN_) 6$]), which is a qualitative reagent to cation Fe^{2+} in a test tube with diluted sulfuric acid. In a test tube with concentrated acid add 1–2 drops of potassium hexacyanoferrate (II) (K_4 [Fe (CN) $_6$] – a reagent to cation Fe^{3+}). Mark the difference in color of solutions in test tubes. How can you explain that during the reaction of iron with sulfuric acid of various concentrations iron ions of various charges are producing?

Experiment 4. Effects of nitric acid on metals

4.1. Pour 1–2 ml of concentrated nitric acid in the first test tube, and in the second – the same volume of diluted one. Place a piece of copper in both test tubes. Observe gas release: in the first test tube – brown (NO_2), the second – colorless (NO). Make up the reaction equations, indicate oxidizing and reducing agent.

4.2. Place two pieces of aluminum, one of which was pretreated with concentrated nitric acid in two test tubes with hydrochloric acid. Observe hydrogen gas release and note in in which test tube does it start earlier and what is the rate of reaction? Find out the cause of this phenomenon.

Experiment 5. Effects of an aqueous solution of alkali on metal

Place a piece of copper, aluminum, iron and zinc in four test tubes, pour into the tubes 1–2 ml of 30% aqueous solution of alkali and heat up. Is there a chemical reaction in all of these test tubes? Make up the equations of occurring reactions, indicate oxidant. What metals react with alkali water solutions? Based on the experiment, range metals by chemical activity in alkaline solutions. Compare the results of the experiment with the values of the standard electrode potentials.

CHAPTER 4 CORROSION OF METALS

4.1 BASIC CONCEPTS AND DEFINITIONS

Corrosion is spontaneous ($\Delta G < 0$) heterogeneous red-ox process of metal interaction with oxidants in environment resulting both in:

- degradation of metals physic-chemical properties,
- dusting of surroundings.

The main reason of corrosion is thermodynamic instability of metal in the presence of oxygen. Corrosion includes two conjugate reactions: the oxidation of metal and the reduction of environment components (O_2, H_2O, H^+ etc.).

Corrosion processes are classified according to various criteria the major of which are represented in Figure 4.1.

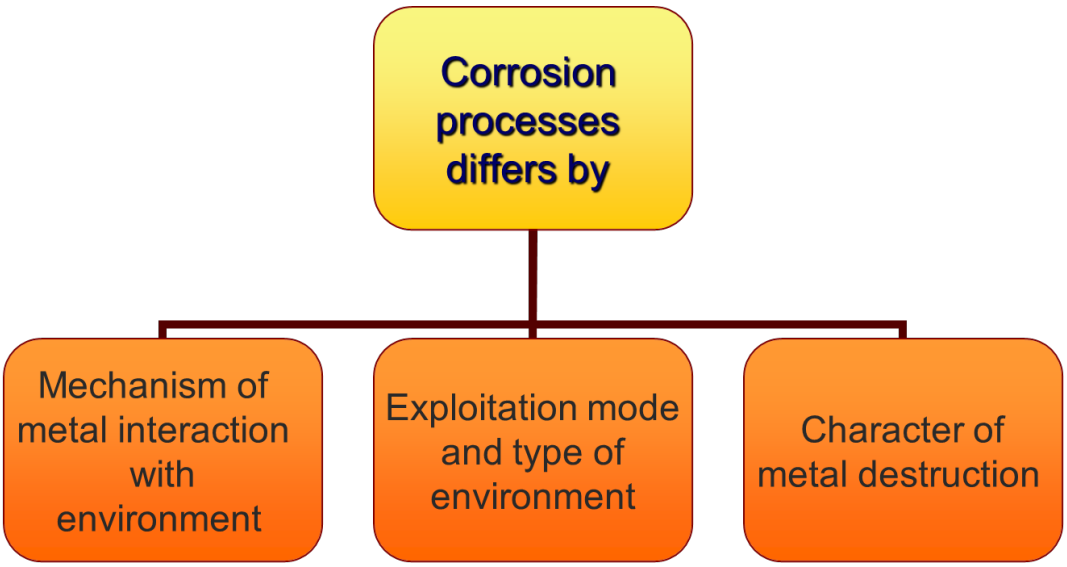


Figure 4.1. Classification of corrosion processes

Chemical corrosion is a direct transfer of electron from metal to an oxidizing agent at their collision, for example:

$$2Fe + O_2 \rightarrow 2FeO.$$

In this case the corrosion products are formed directly on the metal surface, which determines the peculiarities of the process. The conditions of chemical corrosion are dry aggressive gases (F_2, Cl_2, NO_2, SO_2 etc.) at high temperatures, and nonconductive media – liquid gases, petroleum, oil etc. (Fig. 4.2).

Electrochemical corrosion occurs in wet conductive media at oxygen presence. There are two conjugate reactions at separate locations on the metal surface:

anodic **–** oxidation of metal *M* accompanied by formation of electrons and metal cation:

$$M \rightarrow M^{z+} + ze;$$

cathodic – reduction of oxidant (depolarizer) *Ox*

$$Ox + ne \rightarrow Red,$$

where *Red* – reductive form of an oxidant.

The electrons are transferred from the anodic to the cathodic sections on a metal surface (Fig.4.2).

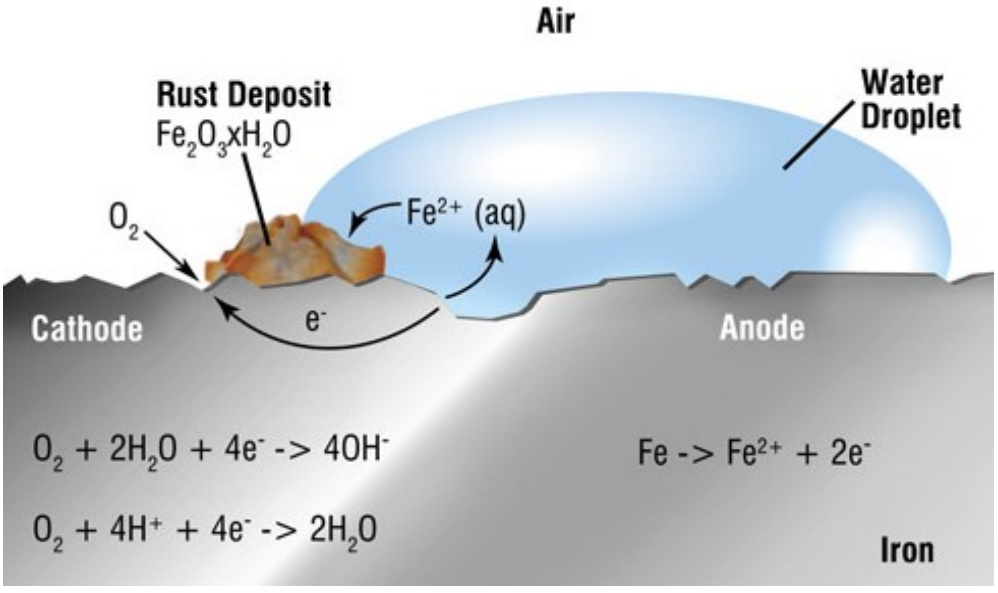


Figure 4.2. Scheme of iron electrochemical corrosion

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion

patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

The secondary reaction in bulk solution is the reaction between the products of metal oxidation and depolarizer reduction:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2,$$

following by further oxidation of iron (II) to iron (III):

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3.$$

The necessary and simultaneously sufficient condition for metal corrosion is the presence in a media a depolarizer those red-ox potential is higher than metal potential: $E(M^{z+}/M) < E(Ox/Red)$.

Such depolarizers commonly are oxygen molecules and hydrogen ions which depending of the medium pH are reduced by reactions:

In acidic media:	In neutral or alkali media:
$O_2 + 4H^+ + 4e \rightarrow 2H_2O;$	$O_2 + 2H_2O + 4e \rightarrow 4OH^-;$
$2H^+ + 2e \rightarrow H_2;$	$2H_2O + 2e \rightarrow H_2 + 2OH^-.$

The potentials of depolarizer reduction may be calculated using Nernst equation or according to the relations:

$$E(H_2/H_2O) = -0{,}059pH,$$

$$E(O_2/H_2O) = 1{,}23 - 0{,}059pH.$$

Biology corrosion occurs by acting of biology factors – micro- (fungi, bacterium, lichen, protozoa) or macro organisms (plants, animals), vital functions of those initiate or catalyze the partial reactions. The bacterium *thiobacillus ferrooxidans* derives its energy by oxidizing Fe^{2+} to the more soluble Fe^{3+}, transferring the electrons to O_2. It also oxidizes the sulfur, producing sulfuric acid. The resulting chemical cocktail has eaten a hole into the pipe (Fig.4.3).

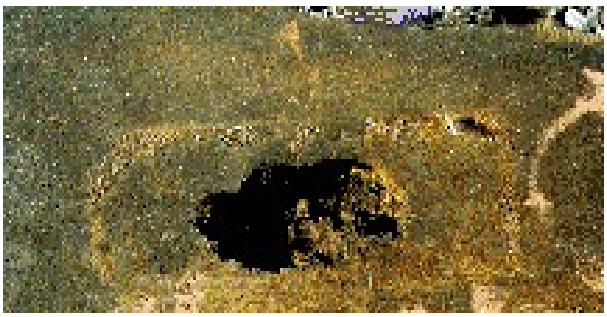


Figure 4.3. Biology corrosion

Classification of corrosion processes by the type of medium.

Atmosphere corrosion is a metal destruction under environmental temperature and humidity, especially under the influence of waste gases (CO_2, SO_2, NO_2, NH_3, HCl), salt particles, coal dust etc.

An industrial atmosphere is characterized by pollution composed mainly of sulfur compounds such as sulfur dioxide (SO_2), a precursor to acid rain, and nitrogen oxides (NO_x), the backbone of smog in modern cities (Fig.4.4 a). Sulfur dioxide from burning coal or other fossil fuels is picked up by moisture on dust particles as sulfurous acid. This is oxidized by some catalytic process on the dust particles to sulfuric acid which settles in microscopic droplets and fall as acid rain on exposed surfaces.

a b

Figure 4.4. Corrosion in industrial (a) and rural atmosphere (b)

The result is that contaminants in an industrial, atmosphere, plus dew or fog, produce a highly corrosive, wet, acid film on exposed surfaces. In addition to the normal industrial atmosphere in or near chemical plants, other corrosive pollutants may be present. These are

usually various forms of chloride which may be much more corrosive than the acid sulfates. The reactivity of acid chlorides with most metals is more pronounced than that of other pollutants such as phosphates and nitrates.

Rural atmospheres are typically the most benign and do not contain strong chemical contaminants, that is unless one is close to a farm operation where byproducts made of various waste materials can be extremely corrosive to most construction materials (Fig.4.4 b). Arid or tropical atmospheres are special variations of the rural atmosphere. In arid climates there is little or no rainfall, but there may be a high relative humidity and occasional condensation. This situation is encountered along the desert coast of northern Africa. In the Tropics, in addition to the high average temperature, the daily cycle includes a high relative humidity, intense sunlight, and long periods of condensation during the night. In sheltered areas, the wetness from condensation may persist long after sunrise. Such conditions may produce a highly corrosive environment.

Normal indoor atmospheres are generally considered to be quite mild when ambient humidity and other corrosive components are under control. However, some combinations of conditions may actually cause relatively severe corrosion problems. While there is no typical contaminant or set of conditions associated with an indoor atmosphere, any enclosed space which is not evacuated or filled with a liquid can be considered an indoor atmosphere. If not ventilated, such an environment may contain fumes, which in the presence of condensation or high humidity could prove to be highly corrosive. Even in the absence of any other corrosive agent, the constant condensation on a cold metallic surface may cause an environment similar to constant immersion for which a component may not have been chosen or prepared for. Such systems are commonly encountered in confined areas close to ground level or, worse, below ground where high humidity may prevail.

Underground corrosion (corrosion in soil) – metal destruction in ground and soil differed by chemical composition, humidity, value of aeration and porosity. Factors that influence soil corrosion are: porosity (aeration); electrical conductivity or resistivity; dissolved salts, including depolarizers or inhibitors; moisture; pH (Table 4.1).

Table 4.1 – Parameters of soil

Resistivity (Ω cm)	Assigned Points	*Redox Potential* (mV)	Assigned Points
<700	10	>100	0
700 – 1000	8	50 – 100	3.5
1000 – 1200	5	0 – 50	4
1200 – 1500	2	<0	5
1500 – 2000	1	*Sulfides*	
> 2000	0	Positive	3.5
pH		Trace	2
0 – 2	5	Negative	0
2 – 4	3	*Moisture*	
4 – 6.5	0	Poor drainage continuously wet	2
6.5 – 7.5	0	Fair drainage generally moist	1
7.5 – 8.5	0	Good drainage generally dry	0
>8.5	3		

Corrosive soils contain chemical constituents that can react with construction materials, such as concrete and ferrous metals, which may damage foundations and buried pipelines. The electrochemical corrosion processes that take place on metal surfaces in soils occur in the groundwater that is in contact with the corroding structure. Both the soil and the climate influence the groundwater composition. The corrosion rate in the clay is always higher than in sand.

Figure 4.5. Soil corrosion

Marine corrosion – in sea water or sea atmosphere characterized by high concentration of Cl^--ions, electric conductivity, wide ionic and gas composition, essential action of biology factors (Fig.4.6).

Figure 4.6. Marine corrosion

A marine atmosphere is laden with fine particles of sea mist carried by the wind to settle on exposed surfaces as salt crystals. The quantity of salt deposited can vary greatly with wind velocity and it may, in extreme weather conditions, even form a very corrosive salt crust. The quantity of salt contamination decreases with distance from the ocean, and is greatly affected by wind currents. The marine atmosphere also includes the space above the sea surfaces where splashing and heavy sea spray is encountered. The equipment exposed to these splash zones are indeed subjected to the worst conditions of intermittent immersion with wet and dry cycling of the corrosive agent.

By the nature of *metal surface destruction*, corrosion is distinguished for uniform, uneven, and some types of local damages (Fig. 4.7).

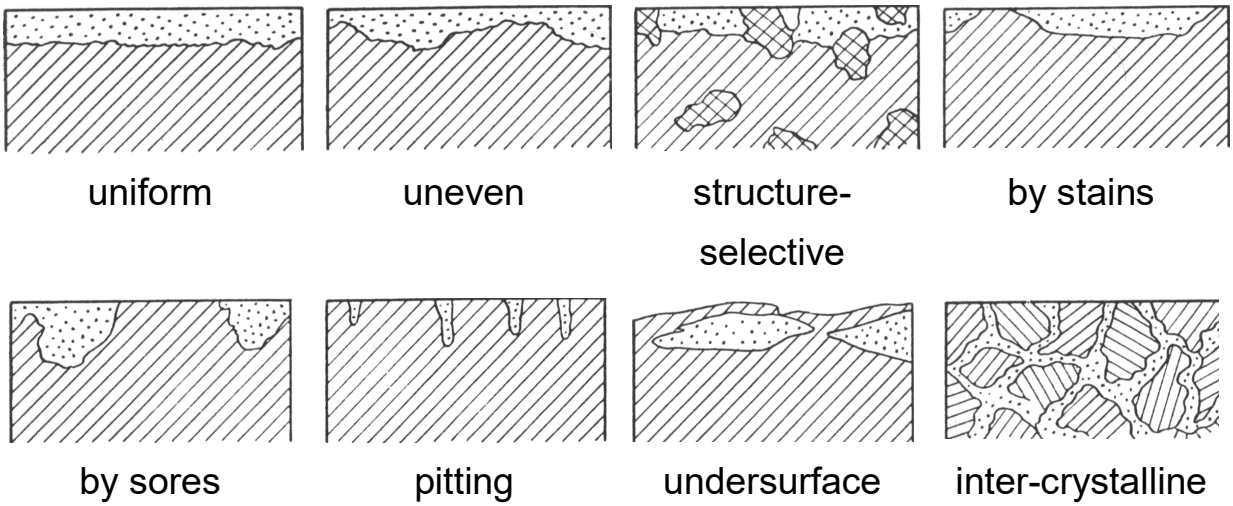


Figure 4.7. Types of corrosion damage

Pitting corrosion. Most metals are covered with a thin oxide film which inhibits anodic dissolution. When corrosion does occur, it sometimes hollows out a narrow hole or *pit* in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal (Fig. 4.8).

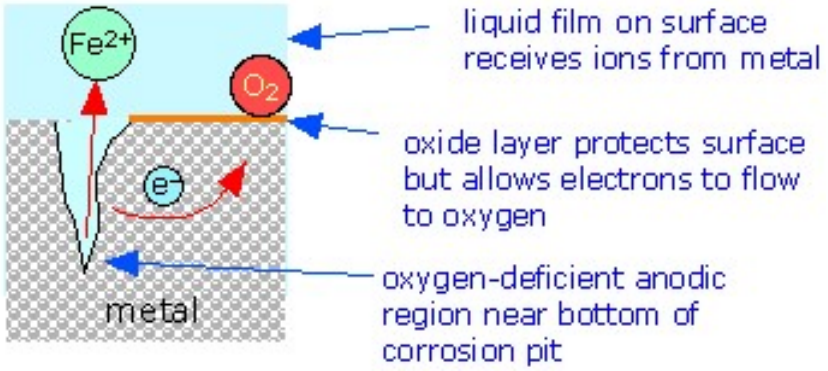


Figure 4.8. Scheme of pit corrosion

Quantitative indexes of corrosion are mass and depth which may be calculated according the equations:

$$K_m = \frac{\Delta m}{S \cdot t},$$

where Δm – change in mass, g;

S – metal surface area, m^2;

t – period of corrosion damage, hour.

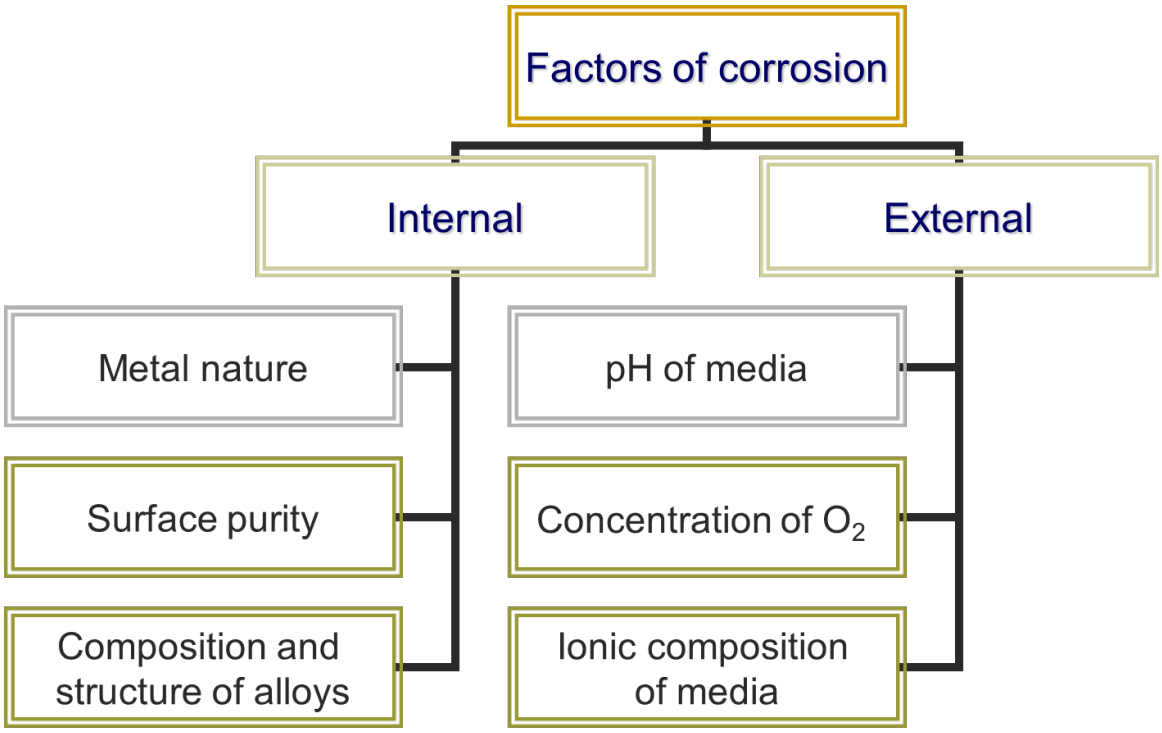
$$K_h = \frac{h}{t},$$

where h – depth of corrosion damage, mm;

t – period of corrosion damage, year.

4.2 FACTORS OF CORROSION

Major factors influencing the corrosion process may be divided in internal and external as presented by following scheme:



Metal nature prerequisites the corrosion destruction according to the rule: the lower is the metal potential the higher will be the corrosion rate of a metal under the same conditions.

The integrity uniform oxide films formed on the surface of some metals protect the latter from the atmosphere action and cause the metal passivity. Metals inclination for passivity is decreased in the range:

Ti > Zr > Ta > Nb > Al > Cr > Be > Mo > Mg > Ni > Co > Fe > Mn > Zn > Cd > Cu.

The corrosion resistance of $Al|Al_2O_3$ ($Ti|TiO_2$, $Zr|ZrO_2$ etc.) under atmosphere conditions is the same as the copper or silver but differs by the mechanism: Cu or Ag thermodynamic stability is higher than Al, Zr or Ti.

The *pH influence* on the metals corrosion rate. Metals may be divided in 5 groups according to the corrosion behavior in aggressive

media of different pH. First group are noble and semi noble metals and their alloys which corrosion rate is low at all pH due to their thermodynamic stability (Fig.4.9 a).

Valve metals are protected by acidic oxide films (MO_2, M_2O_5, MO_3) and exhibit high corrosion resistance in acidic and neutral media, but their corrosion accelerates in alkali ones because of oxide dissolution (Fig.4.9 b), for example:

$$WO_3 + 4OH^- \rightarrow WO_4^{2-} + 2H_2O,$$

$$M - ze \rightarrow M^{z+},$$

$$O_2 + 4e + 2H_2O \rightarrow 4OH^-.$$

Amphoteric metals exhibit corrosion resistance only in neutral media due to insoluble hydroxides or oxides formation. In acidic and alkali environment their corrosion accelerates because of oxide or hydroxide dissolution (Fig.4… c), for example:

In acidic media: $M - ze \rightarrow M^{z+}$

$$O_2 + 4e + 4H^+ \rightarrow 2H_2O$$

In neutral media:

$M - ze \rightarrow M^{z+}$

$O_2 + 4e + 2H_2O \rightarrow 4OH^-$

$M^{z+} + 2OH^- \rightarrow M(OH)_z\downarrow$

In alkali media:

$M(OH)_z\downarrow + zOH^- \rightarrow [M(OH)_{2z}]^{z-}$

Such metals as copper, nickel, cobalt, cadmium and their alloys (Fig.4.9 d) are stable both in neutral and alkali media due to insolubility of hydroxides $M(OH)_2$ or oxides MO forming in the secondary reaction. The rate of metals corrosion in acidic media increases rapidly because of dissolution oxide or hydroxide surface films.

Polyvalent metals exhibit more complex corrosive behavior. The corresponding reactions are shown in Fig.4.9 e. It should be noted their resistance in a neutral and weakly alkaline environment and acceleration of corrosion in acidic. In a strongly alkaline environment, an increase in

the corrosion rate is associated with the dissolution of amphoteric hydroxides formed by metals of a higher oxidation state.

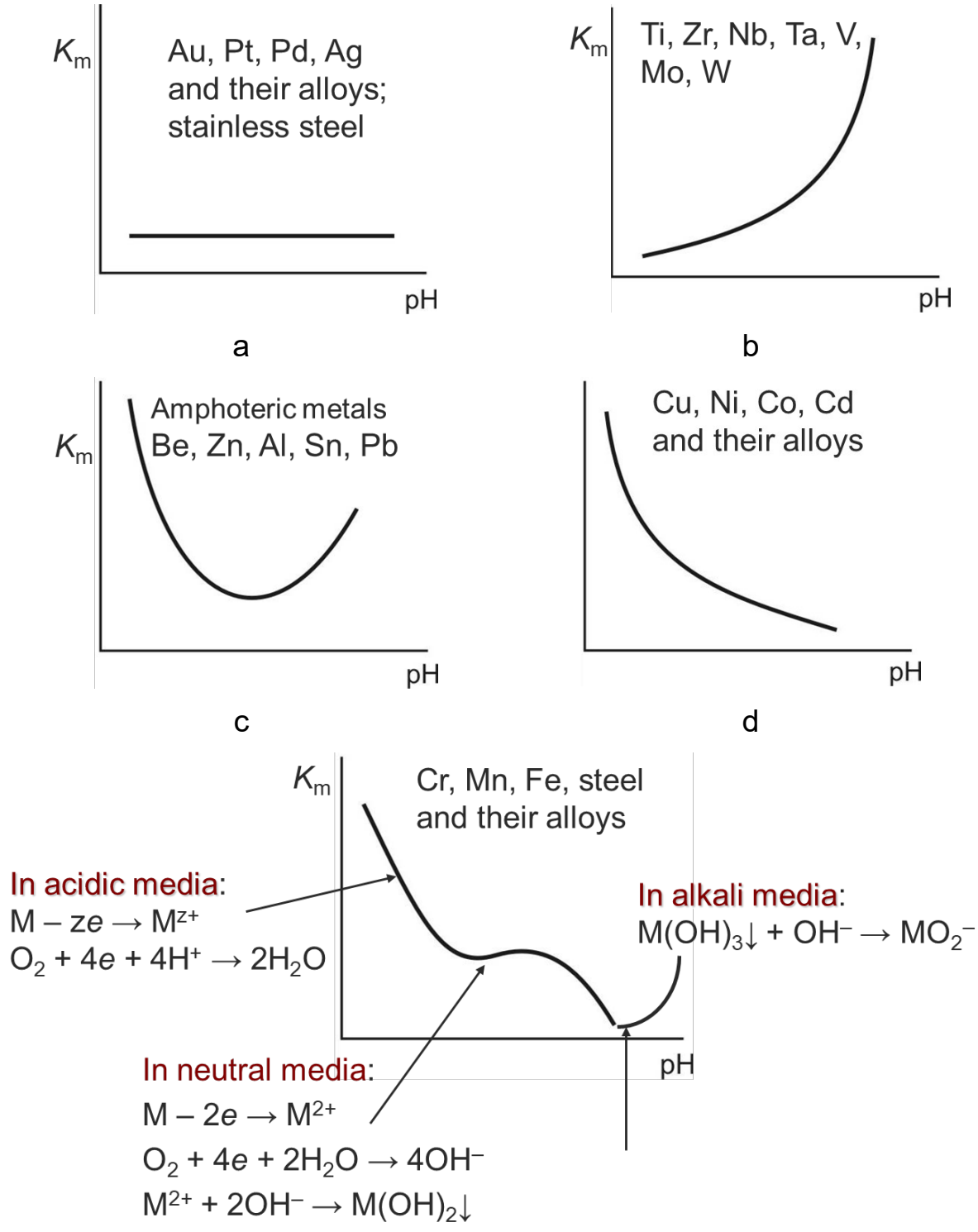


Figure 4.9. Effect of environment pH on corrosion rate of metals

The influence of O_2 concentration on the corrosion rate depends first of all on the nature of metal (Fig.4.10), and may be reflected by kinetic equations for different media:

Acidic $v = k \cdot c(O_2) \cdot c(H^+)^4$,

Neutral and alkali $v = k \cdot c(O_2) \cdot c(H_2O)^2$.

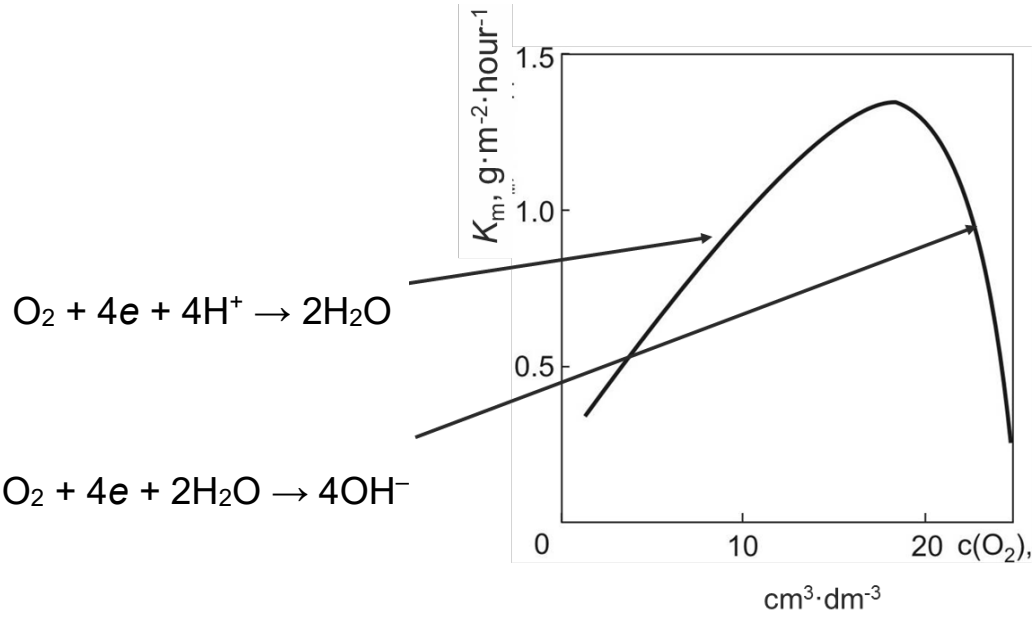


Figure 4.10. The oxygen influence on the corrosion behavior of metals

These equations reflect the possibility of some metals passivation in the excess of oxygen especially in neutral and alkali media.

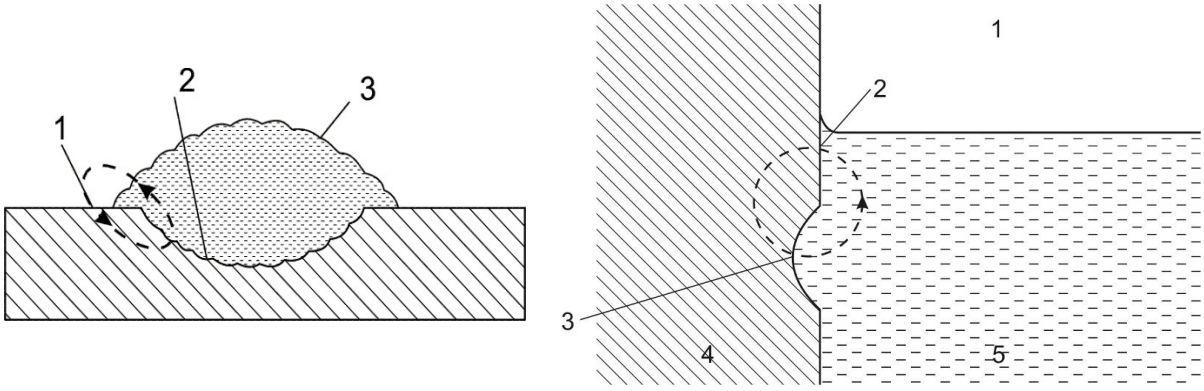
As was shown for pairs of differential aeration (Fig.4.11) cathodic reaction (1) occurs on the side of high concentration of O_2, and anodic one (2) – on the side of low concentration of O_2 under the lay of corrosion products (3).

Passivation of metals in high oxygenation environment is associated with oxide or hydroxide film formation.

Corrosion activators accelerate the corrosion process.

Anions which destroy oxide passive films on metal surface of prevent passivation. The activation ability of anions is decreasing in the range

$$Cl^- > SO_4^{2-} > ClO_4^- > Br^- > I^- > F^-.$$



a b

Figure 4.11. Pairs of differential aeration under the water drop (a) and under the waterline (b): 1 – air, 2 – cathodic reaction, 3 – anodic reaction, 4 – metal, 5 – sea water.

Compounds which form soluble corrosion products with metal ions in secondary reactions:

NH_3, F^-, CN^-, CNS^-, for amphoteric metals – OH^-

The cations of metals with different oxidation number promote the side reaction of cations recharge:

$$Fe^{3+} + e \rightarrow Fe^{2+},\ E^0(Fe^{3+}/\ Fe^{2+})=0.77V$$

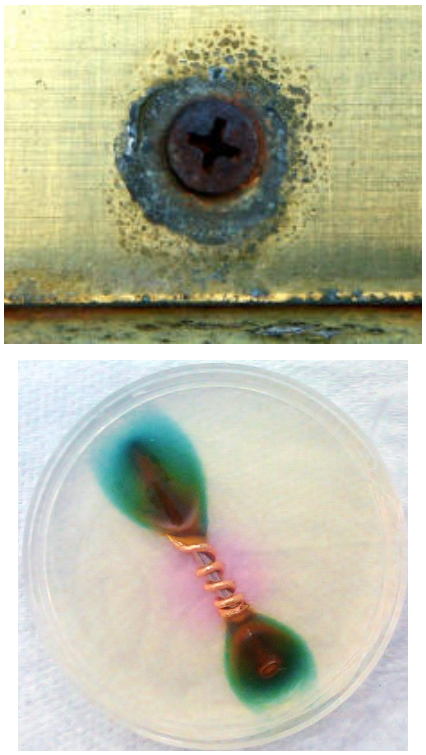
The cations of less active metals which are the addition oxidizing agents for corroding metal:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu,$$

$$-0.44\ V \qquad +0.34\ V.$$

Galvanic corrosion (also called **bimetallic corrosion**) is an electrochemical process in which one metal corrodes preferentially when it is in electrical contact with another, in the presence of an electrolyte. A similar galvanic reaction is exploited in primary cells to generate a useful electrical voltage to power portable devices. Corrosion of an iron nail wrapped in bright copper wire, showing cathodic protection of copper; a ferroxyl indicator solution shows colored chemical indications of two types

of ions diffusing through a moist agar medium (Fig.4.12 a). Iron corrodes producing Fe^{2+} cations in anodic reaction which change the color of indicator to blue. On the copper surface, OH^- ions are generated in the cathodic reaction of oxygen reduction, and indicator becomes pink.
The following metal in the same group accelerates the corrosion of previous metal (Fig. 4.12 b). The metal of the following group accelerates the corrosion of metals in previous one. The metals of the same group may be connected in the construction, device etc.



Group	Metals
I	Mg
II	Zn, Al and their alloys, Cd
III	Fe, mild steels, Sn, Pb
IV	Ni, Cr, chromium and Ni containing steels
V	Cu-Ni, Cu-Sn, Cu-Zn alloys, Cu, Ag
VI	Pt, Pd, Au and their alloys

a b

Figure 4.12. Galvanic corrosion pairs

4.3 CONTROL TASKS

Write the anodic and cathodic reactions occurring under corrosion of metal given in your variant (table 4.2) in the presence of oxygen in different media:

- neutral (pH = 7);
- acidic (pH = 3);
- alkali (pH = 10).

Table 4.2. − Variant of problem

Variant	Metals	Variant	Metals	Variant	Metals
1	Li, Zn, Ag	9	Mg, Co, Re	17	Ba, Zn, Sb
2	Na, Cd, Cu	10	Sr, Ni, Cu	18	Ca, Cr, Re
3	Ba, Fe, Hg	11	Ca, Mo, Ru	19	Na, Ga, Cu
4	Ca, Ni, Au	12	Rb, Sn, Rh	20	Sr, Fe, Hg
5	Sr, Mn, Bi	13	Li, Pb, Ag	21	Cs, In, Ag
6	K, Co, Pd	14	Be, W, Os	22	Rb, Mn, Tc
7	Cs, Cd, Sb	15	Mg, Al, Pd	23	Li, Ti, Ru
8	Ba, Tl, Bi	16	K, Mn, Ge	24	Sr, Pb, Ge

4.4 EXPERIMENTAL PART

Experiment 1. Influence of metal contacting the speed of corrosion processes

Make three tube piece zinc and pour 1–2 ml sulfuric acid. Write an equation of reaction that occurs. Touch piece zinc in a copper wire tube, the second – the iron, the third – aluminum. Watch the intensity and location of hydrogen in each case. Explain these phenomena in terms of the galvanic couple formation and specify conclusions. On the surface of which contacting metal anode reaction is processing, and on the surface of which – cathode? Write the anodic and cathodic reactions of the corrosion process. How will change the corrosion rate by increasing the pH to 7?

Experiment 2. Corrosion in a neutral environment

2.1. Electrochemical heterogeneity steel surface

Clean surface of the steel plate, rinse under running water and dry filter paper. Then place on a plate filter paper soaked with complex ferroxyl indicator.

The composition ferroxyl indicator is: water, sodium chloride, phenolphthalein and $K_3[Fe(CN)_6]$. The latter is a reagent for Fe^{2+} ion and forms an intense blue color in it presence. Phenolphthalein becomes pink in the presence of hydroxide ions (OH^-).

After 2–3 minutes describe the occurrence, distribution and dimensions of lots of different colors. Explain observations, make a diagram of the corrosion process (write reactions occurring at the "anode" and "cathode" areas of the sample surface).

2.2. Effect of ionic composition environment on the corrosion of aluminum

In two porcelain cups place on aluminum grains. In one of them pour the solution of copper (+2) chloride, and the second – copper (+2) sulfate. In the case precipitation of copper, gassing and bleaching solution is faster? Make the equation responses. Explain anion which accelerates the corrosion of aluminum? Why? What gas is released, and why? What environment – sea or river water – is more aggressive? Why?

Experiment 3. Corrosion behavior of steel in active and passive state

Steel plate clean sandpaper, wash with running water and then soak for activation in hydrochloric acid solution for 2–3 minutes and then rinse with water. In the test tube pour a solution of sodium chloride, add a few drops of $K_3[Fe(CN)_6]$ and dip it a steel plate. Watch the appearance of blue precipitate. Then rinse with water and this plate is dip (in a fume hood) for 2–3 minutes in concentrated nitric acid, then rinse with water. Sodium chloride solution with $K_3[Fe(CN)_6]$ in test tube replace with fresh and repeat the experiment and observation. Explain the difference in the

corrosion behavior of steel after treatment with dilute hydrochloric acid and concentrated nitric and mechanism of treatment on the corrosion rate.

Experiment 4. Analysis of differential aeration elements

Iron plate clean sandpaper, wash under running water and dry filter paper. On the surface apply a drop solution ferroxyl indicator. Watch the color drops. Explain why there is a drop in the center of the blue, and the edges – pink?

Experiment 5. Corrosion of metals in an alkaline environment

In three test tubes pour a 30% solution of NaOH. One of them put a piece of zinc, the second – copper, in the third – aluminum. To accelerate the process, the reaction mixture in the tube warm up. Watch metals subject to corrosion in an alkaline environment, which gas is released at the same time? Write the reaction. What substance serves as depolarizer in these processes?

Experiment 6. Effect of pH on the rate of corrosion of steel

Pour three cups of 20 ml NaCl, add the first cup 20 ml H_2O; the second – 20 ml HCl; the third – 20 ml NaOH. At all glass add a few drops of $K_3[Fe(CN)_6]$, and dip the steel wires in them. Watch the rate of appearance of blue sediment in each glass and make a conclusion about the dependence of the corrosion rate of the steel on the pH.

Major constants

Name	Symbol	Value
Faraday constant	F	96500 Cl·mol^{-1}; 26.8 A·hour·mol^{-1}
Avogadro constant	N_A	6.022·10^{23} mol^{-1}
Elementary charge	e	1.602·10^{-19} Cl
Gas constant	R	8.314 J·mol^{-1}·K^{-1}
Electric constant	ε_0	8.854·10^{-12} F·m^{-1}
Atomic mass unit	μ	1.660·10^{-27} kg
Molar volume of ideal gas at T_0 = 273,15 K; p_0 = 101325 Pa	V_m	22.414·10^{-3} m^3·mol^{-1}

Derivatives of physical parameters

Parameter	Name	Symbol	Definition
Energy, work	Joule	J	m^2·kg·s^{-2}
Pressure	Pascal	Pa	m^{-1}·kg·s^{-2}
Electric charge, quantity of electricity	Coulomb	C	s·A
Electric potential, voltage, electromotive force	Volt	V	m^2·kg·s^{-3}·A^{-1}
Electric capacity	Farad	F	m^{-2}·kg^{-1}·s^4·A^2
Electric resistance	Ohm	Ω	m^2·kg·s^{-3}·A^{-2}
Electric conductance	Siemens	S	m^{-2}·kg^{-1}·s^3·A^2

CHAPTER 5 CORROSION PROTECTION

5.1 BASIC CONCEPTS AND DEFINITIONS

Active corrosion protection. The aim of active corrosion protection is to influence the reactions which proceed during corrosion, it being possible to control not only the metal construction and the corrosive agent but also the reaction itself in such a manner that corrosion is avoided. Examples of such an approach are: the development of corrosion-resistant alloys the addition of inhibitors to the aggressive medium.

Passive corrosion protection. In passive corrosion protection, damage is prevented by mechanically isolating the metal from the aggressive corrosive agents (by using protective layers, films or other coatings). However, this type of corrosion protection changes neither the general ability of the metal to corrode, nor the aggressiveness of the corrosive agent. If the protective layer, film etc. is destroyed at any point, corrosion may occur within a very short time. The passive corrosion protection methods may be permanent and temporary.

Permanent corrosion protection. The purpose of permanent corrosion protection methods is mainly to provide protection at the place of use. The stresses presented by climatic, biotic and chemical factors are relatively slight in this situation.

The protective coating isolates the metallic surfaces from the aggressive media, such as moisture, salts, acids etc: tin, nickel, copper plating; galvanization (Zn); oxide coating; enameling.

Temporary corrosion protection. The stresses occurring during transport, handling and storage are much greater than those occurring at the place of use. The main temporary corrosion protection methods:

- Solvent-based anticorrosion agents;
- Water-based anticorrosion agents;

- Corrosion-protective oils without solvent;
- Dipping waxes.

Material selection – selection of proper material for a particular corrosive service: metallic [metal and alloy]; nonmetallic [rubbers (natural and synthetic), plastics, ceramics, carbon and graphite, and wood]. The examples of metal stability in media of different composition is presented in the Table 5.1.

Table 5.1 – Proper metals for different media

№	Environment	Proper material
1	Nitric acid HNO_3	Stainless steels
2	Sodium hydroxide NaOH	Nickel and nickel alloys
3	Hydrofluoric acid HF	Monel (Ni-Cu)
4	Hot hydrochloric acid HCl	Hastelloys (Ni-Cr-Mo)
5	Dilute sulfuric acid H_2SO_4	Lead
6	Nonstaining atmospheric exposure	Aluminium
7	Distilled water	Tin
8	Hot strong oxidizing solution	Titanium
9	Ultimate resistance	Tantalum
10	Concentrated sulfuric acid H_2SO_4	Steel

5.2 ALLOYING OF METALS

Introduction to the composition of the metal components, which increase the tendency to passivation, reduce the cathodic or anodic activity of the alloy, prevent structural corrosion. Alloying additives are

divided into macro (main) – 5–20% and micro (minor) – up to 3%. Other than Ni, Cr and C, the following alloying elements may also present in stainless steel: Mo, N, Si, Mn, Cu, Ti, Nb, Ta and/or W.

Main alloying elements are Cr, Ni and C.

Carbon forms steel structure which differs by the grain sizes (Fig. 5.1).

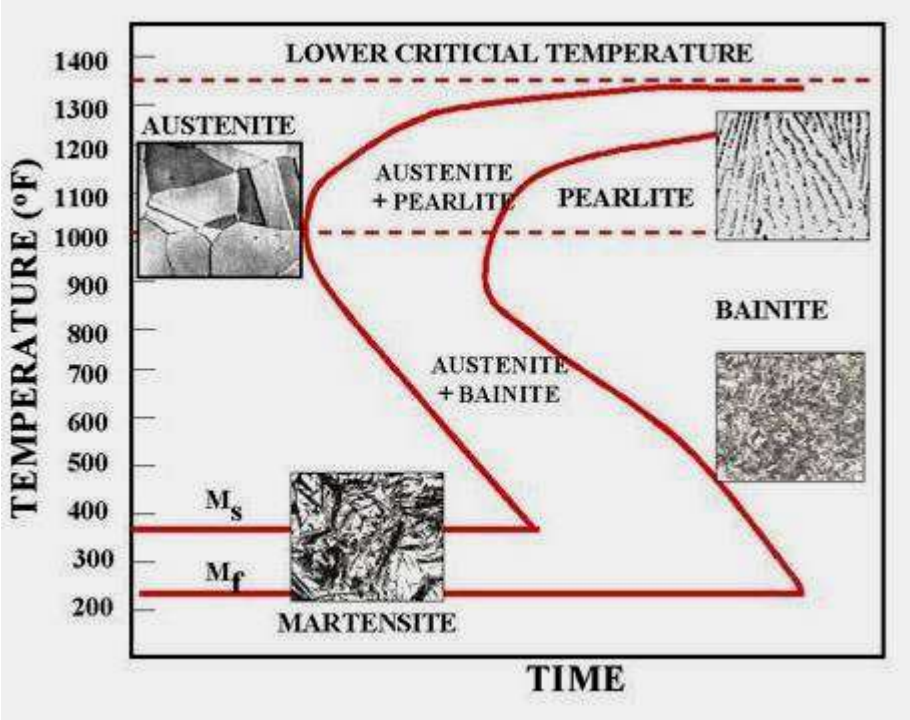


Figure 5.1. Steel structure depending on the temperature

Chromium. Minimum concentration of Cr in a stainless steel is 12–14 wt.%. Note that the affinity of Cr to form Cr-carbides is very high. Chromium carbide formation along grain boundaries may induce intergranular corrosion (Fig.5.2).

Nickel added to produce austenitic or duplex stainless steels. These materials possess excellent ductility, formability and toughness as well as weld-ability. Nickel improves mechanical properties of stainless steels servicing at high temperatures. Nickel increases aqueous corrosion resistance of materials.

Minor alloying elements

Manganese is an austenitic forming element. Mn when necessary can be used to substitute Ni. Concentration of Mn in stainless steel is usually 2–3% wt.

Molybdenum is ferrite forming element. It is added to increase pitting corrosion resistance of stainless steel (2–4%). Mo improves mechanical properties of stainless steel at high temperature. Increase aqueous corrosion resistance of material exposed in reducing acid.

Tungsten is added to increase the strength and toughness of martensitic stainless steel.

Nitrogen (up to 0.25%) stabilizes austenitic structure. It increases strength and corrosion resistance. Increases weld ability of duplex SS.

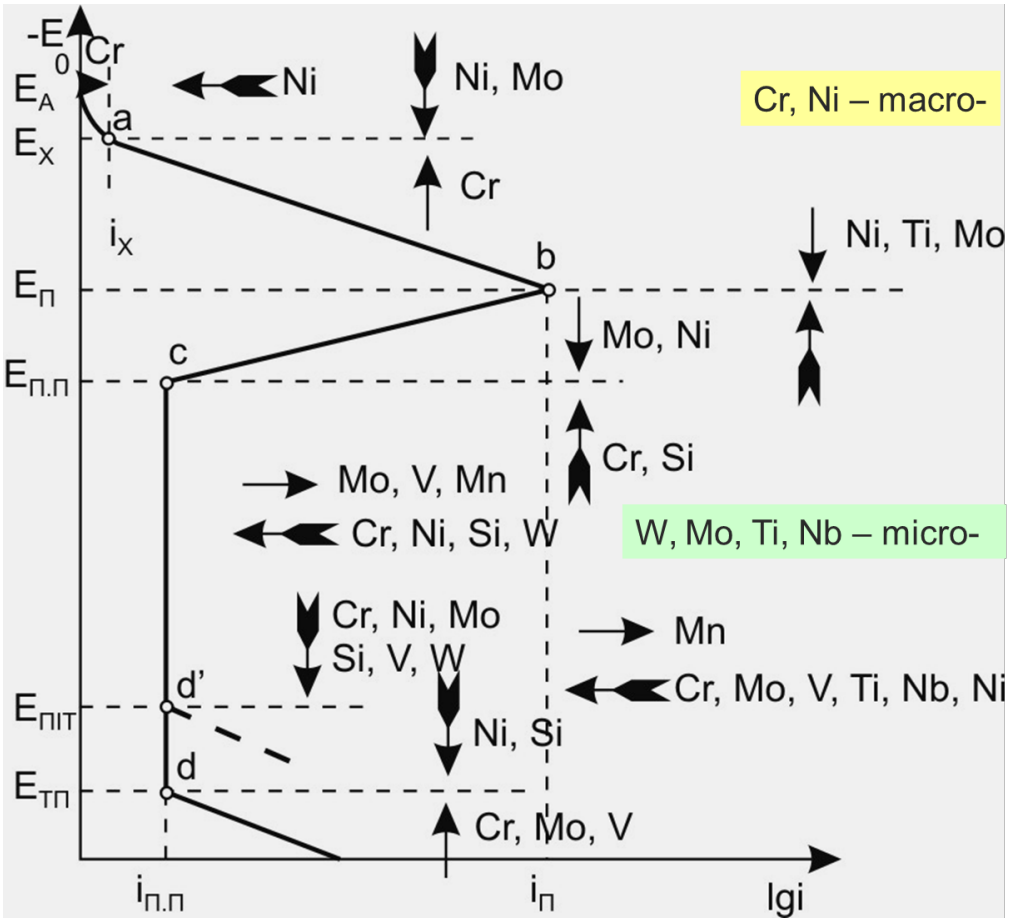


Figure 5.2. Corrosion diagram of stainless steel

Titanium, **Niobium** and **Tantalum** are added to stabilize stainless steel by reducing susceptibility of the material to intergranular corrosion.

Copper is added to increase corrosion resistance of stainless steel exposed in environment containing sulfuric acid.

Silicon reduces susceptibility of SS to pitting and crevice corrosion.

Surface treatment. Polishing of the surface thereby reducing the rate of corrosion by reducing the roughness and specific surface area.

5.3 ALTERATION OF ENVIRONMENT

Typical changes in medium are:

- Lowering temperature – but there are cases where increasing T decreases attack: hot, fresh or salt water is raised to boiling T and result in decreasing O_2 solubility with T.
- Decreasing velocity. Exception is metals and alloys that passivate (stainless steel) generally have better resistance to flowing mediums than stagnant.
- Avoid very high velocity because of erosion-corrosion effects.

Removing oxygen or oxidizers can be carried out by various methods.

Chemical method is grounded on the usage of reducing agents:

$$O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4 \text{ or } O_2 + N_2H_4 \rightarrow H_2O + N_2.$$

Deaeration may be realized by inert gases (N_2, Ar) blowing or vacuum treatment. However, it can't be recommended for active-passive metals or alloys. These materials require oxidizers to form protective oxide films.

Neutralization of the environment. The change in the concentration of H^+ ions by neutralization of the with soda or slaked lime:

$$2H^+ + Ca(OH)_2 \rightarrow Ca^{2+} + 2H_2O.$$

Removing activators from the environment using reagent method:

$$2Cl^- + Pb^{2+} \rightarrow PbCl_2,$$

or distillation, or using ion exchange membranes (Fig.5.3). However, for materials that exhibit passivity, effect is normally negligible.

The main approach is to *reduce the temperature*. In some cases, as the temperature rises, the corrosion rate drops: when the electrolyte evaporates or the oxygen concentration decreases.

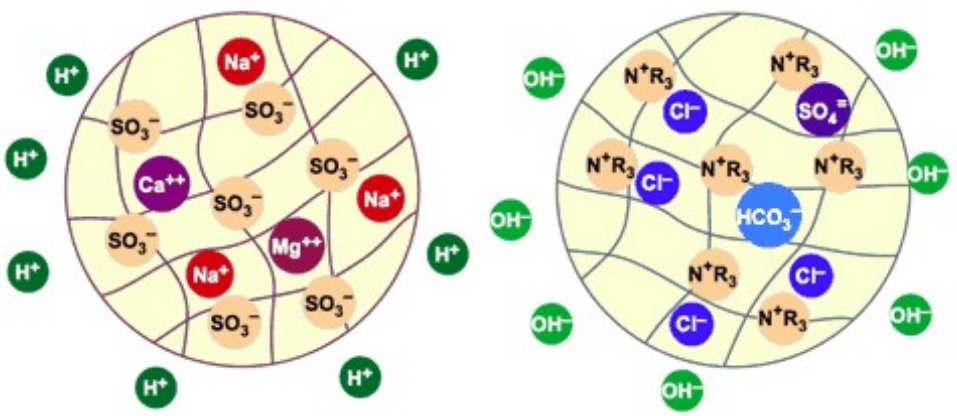


Figure 5.3. Ion-exchange membrane purification

5.4 PROTECTIVE COATINGS

Coatings provide barrier between metal and environment, and may act as sacrificial anode or release substance that inhibits corrosive attack on substrate (Fig.5.4).

- Metal coatings:
  - Sacrificial – Zn, Al, Mn on steel. Exposed substrate will be cathodic and will be protected (Fig.5.4 a).
  - Noble – Ag, Cu, Ni, Cr, Sn, Pb on steel (Fig.5.4 b). Should be free of pores/discontinuity. Disintegration of coating creates small anode/large cathode leading to rapid attack at the damaged areas (.
  - Application of coatings – hot dipping, flame spraying, cladding, electroplating, vapor deposition, etc.

- Surface modification – to structure or composition by use of directed energy or particle beams, ion implantation and laser processing.

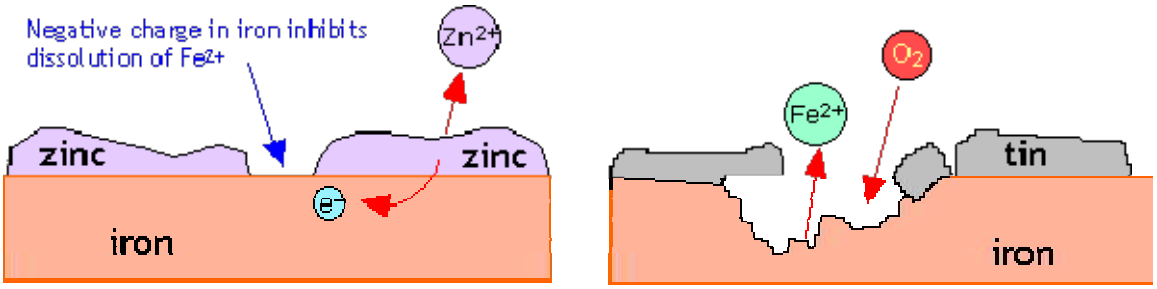


Figure 5.4. Anodic (sacrificial) and cathodic (noble) coatings

The reactions occuring in both systems of coatings depends on their nature.

Anodic (sacrificial):

$Zn - 2e \rightarrow Zn^{2+}$,

$Fe \mid O_2 + 2H_2O + 4e \rightarrow 4OH^-$.

Cathodic:

$Fe - 2e \rightarrow Fe^{2+}$,

$Sn \mid O_2 + 2H_2O + 4e \rightarrow 4OH^-$.

Inorganic coatings are: cement, glass, ceramic, chemical conversion coatings.

Chemical conversion coatings may be formed by:

Anodizing (Al in H_2SO_4)

anode: $2Al + 3H_2O - 6e \rightarrow Al_2O_3 + 6H^+$

cathode: $2H^+ + 2e \rightarrow H_2$

Phosphatyzing $2Fe + 2H_3PO_4 + 3H_2O_2 \rightarrow 2FePO_4 + 6H_2O$

Oxide coating $Fe + 2NaNO_2 + H_2O \rightarrow FeO + 2NO + 2NaOH$

Chromate $3Fe + K_2Cr_2O_7 + H_2O \rightarrow 3FeO + Cr_2O_3 + 2KOH$

Organic coatings: paints, lacquers, varnishes.

Coating liquid generally consists of solvent, resin and pigment.

The resin provides chemical and corrosion resistance, and pigments may also have corrosion inhibition functions. Application must be to clean and dry surfaces that have been properly prepared.

Many paints, coatings and high-performance organic coatings have been developed as a need to protect equipment from environmental damage. Of prime importance in the development of protective coatings was the petroleum industry that produced most of the basic ingredients from which most synthetic resins were developed.

5.5 CORROSION INHIBITORS

- The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied.
- In the oil production and processing industries, inhibitors have always been considered to be the first line of defense against corrosion.
- A synergism, or cooperation, is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations.
- Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection.
- Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film.
- Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating. Inhibitors slow corrosion processes by either:
    - Increasing the anodic or cathodic polarization behavior;
    - Reducing the movement or diffusion of ions to the metallic surface;

■ Increasing the electrical resistance of the metallic surface.

Inhibitors have been classified by their functionality: passivating; cathodic; organic; precipitation; volatile corrosion inhibitors.

Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of above inhibitors:

- Oxidizing anions ($Cr_2O_7^{2-}$, NO_3^-, NO_2^-, MoO_4^{2-}, WO_4^{2-}), that can passivate steel in the absence of oxygen, for example:

$$2Fe + 2CrO_4^{2-} + 2H_2O \rightarrow Fe_2O_3 + Cr_2O_3 + 4OH^-.$$

- Non-oxidizing ions (PO_4^{3-}, SiO_3^{2-}, CO_3^{2-}) that require the presence of oxygen to passivate steel, for example:

$$2Fe + 2SiO_3^{2-} + O_2 + 2H_2O \rightarrow 2FeSiO_3 + 4OH^-.$$

These inhibitors are the most effective and consequently the most widely used. Chromate based inhibitors are the least expensive and were used until recently in a variety of applications: recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers. Na_2CrO_4 in concentrations of 0.04–0.1% was used for these applications. At higher temperatures or in water with Cl^- concentrations above 10 ppm higher concentrations are required. If necessary, NaOH is added to adjust the pH to a range of 7.5–9.5. If the concentration of chromate falls below 0.016% corrosion will be accelerated.

In general, passivation inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. For this reason, it is essential that monitoring of the inhibitor concentration be performed.

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms as:

- Cathodic poisons – compounds of As and Sb work by making the recombination and discharge of H_2 more difficult.
- Cathodic precipitates – some cations Ca^{2+}, Zn^{2+}, Mg^{2+} may be precipitated as oxides to form a protective layer on the metal.
- Oxygen scavengers – help to inhibit corrosion by preventing the cathodic depolarization caused by O_2. The most commonly used oxygen scavenger at ambient temperature is Na_2SO_3.

Both anodic and cathodic effects are observed in the presence of *organic inhibitors* but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually protect the metal by forming a hydrophobic film on the metal surface (Fig.5.5). The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.

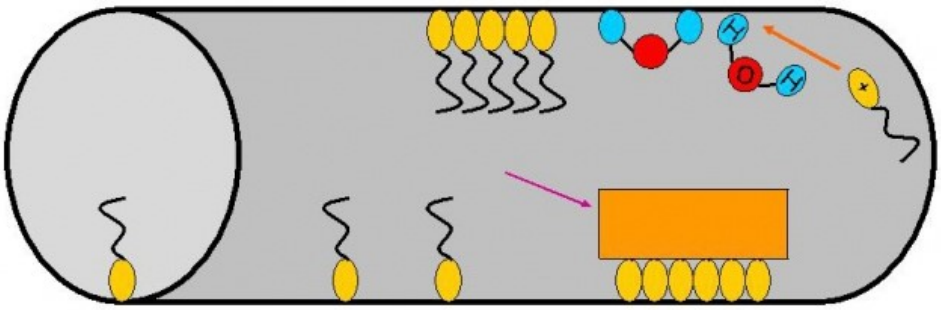


Figure 5.5. Organic inhibitors acting

Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors (amines) or anionic ones (sulfonates) will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

For any specific inhibitor in any given medium there is an optimal concentration: 0.05% sodium benzoate, or 0.2% sodium cinnamate, is effective in water with a pH of 7.5 and containing either 17 ppm sodium

chloride or 0.5% by weight of ethyl octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds (morpholine or hydrazine), are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic CO_2 or by shifting surface pH towards less acidic and corrosive values. In closed vapor spaces (shipping containers) volatile solids (salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine) are used. On contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions.

Control/prevention: reduce applied stress level; remove residual tensile stress (internal stress); lowering oxidizing agent and/or critical species from the environment; add inhibitor; use more resistant alloys; cathodic protection.

Rational design is one of major protection technique (Fig.5.6). Avoid sharp corners – paint tends to be thinner at sharp corners and often starts to fail. Provide for easy drainage (esp tanks) – avoid remaining liquids collect at bottom. Electrogalvanized steel (zinc coated steel) is resistant against concentrated sulfuric acid. But if remaining liquid is exposed to air, acid tend to absorb moisture, resulting in dilution and rapid attack occurs. Avoid hot spots during heat transfer operations – localized heating and high corrosion rates. Hot spots also tend to produce stresses. Design to exclude air – except for active-passive metals and alloys because they require O_2 for protective films.

Most general rule: AVOID HETEROGENEITY!!!

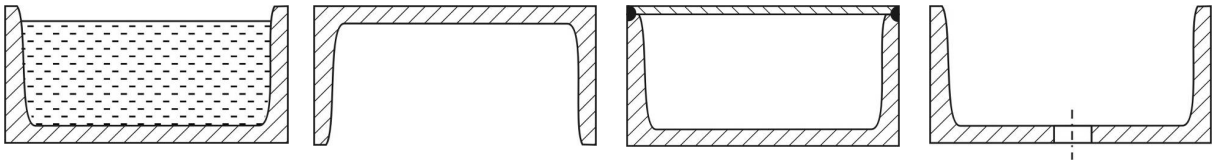


Figure 5.6. The accumulation of moisture in the structural elements (a) and examples of its elimination due to: effective placement (b), isolation from the medium (c) and removal through the drainage holes (d).

5.6 ELECTROCHEMICAL PROTECTION

Electrochemical protection is anodic and cathodic and is used either alone or in combination with other methods of protection.

Anodic protection is used only for passivating metals and alloys. It requires complex potential monitoring equipment and a constant medium composition. The protected object (2) is connected to the positive pole of the direct current source (1), while the metal enters a passive state, using the counter cathode (3). The control of anodic potential performed using reference electrode (4).

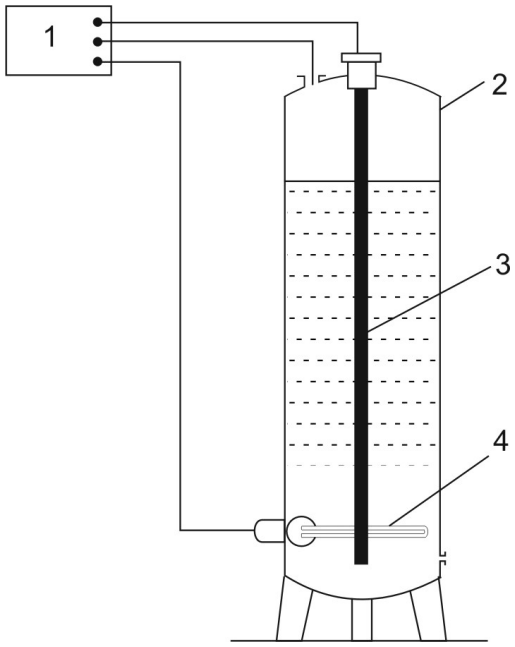


Figure 5.7. Scheme of anodic protection.

When organizing anodic protection, the following general principles are considered:

• the ratio of the surface area protecting, and the cathode is 10^3–10^4;

• protected metal must have a zone of stable passive state greater than 50 mV;

• Through the surface of the structure, the electric current must flow freely, which guarantees its access to each structural element that is in contact with the aggressive medium;

• the environment should have a stable composition and high electrical conductivity.

The effectiveness of anodic protection is estimated by the coefficient of protection K_P:

$$K_P = \frac{i_{cor}}{i_{PP}},$$

where i_{cor} – corrosion current density without protection;

i_{PP} – current density in common passive state.

Anodic protection is applicated to reduce general corrosion, but with the right choice of protective potentials, selective corrosion of ferrite, intergranular corrosion and corrosion cracking of chromium steels, and pitting corrosion of stainless steels can be prevented.

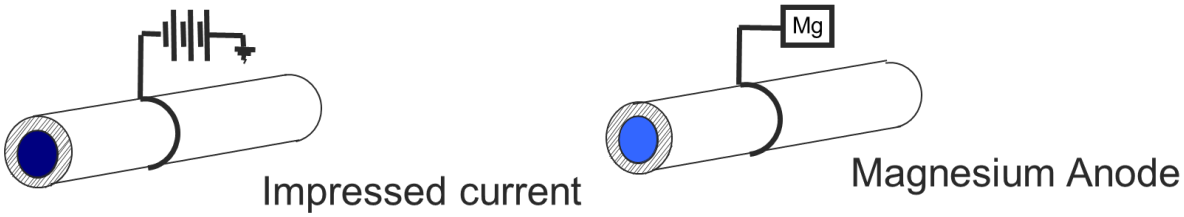
Anodic protection is used in the following cases: for carbon steels in a liquid mineral fertilizer; for autoclaves made of carbon steel at alkaline cellulose cooking; carbon and alloy steels in concentrated sulfuric acid; titanium, zirconium when working in highly aggressive environments. It is also used to reduce the pollution of the aggressive environment by corrosion products.

The main disadvantage of anodic protection is the high cost of equipment and the need for trouble-free operation of a complex control and measuring apparatus to maintain the protective potential in a fairly narrow range in order to reduce the probability of pitting or transpiration.

Cathodic protection

Impressed Current cathodic protection (ICCP) (Fig. 5.8 a)

- Involves the use of an external power source – metal to be protected is made cathodic to its surroundings – inert anodes used which are virtually non-consumable – insulated from structure.
- Early anodes made from scrap steel but most modern ICCP systems use lead silver alloy, titanium or niobium.
- Has been used in the protection of steel reinforcement in concrete
- The use of modern electronics makes the system self-regulating.
- Very costly to run – mainly used in marine applications – oil rigs – large anodes placed on sea bed approximately 100 m away.



a b

Figure 5.8. Typical protection for a buried pipeline by:

a – impressed current; b – sacrificial anode

ICCP protective effect is estimated by following indexes:

- *Protective affect Z*, (%)

$$Z = \frac{k_m^0 \quad k_m^1}{k_m^0} \quad 100\ \%,$$

where k_m^0 i k_m^1 – metal mass corrosion indexes without protection and at ICCP consequently;

- *Protective coefficient* k_P which reflects decreasing in mass loss per unit protection current i_C:

$$k_P = \frac{\Delta m_0 \quad \Delta m_1}{i_C},$$

where Δm_0 i Δm_1 – metal mass loss, g, without protection and at ICCP consequently; i_C – protective current density, A/m^2.

Application of CP

Engineering and Design, Cathodic Protection, requires both cathodic protection (CP) and coatings, regardless of soil or water resistivity, for the following buried or submerged ferrous metallic structures:

- Natural gas and propane piping;
- Liquid fuel piping;
- Oxygen piping;
- Underground storage tank (UST) systems;
- Fire protection piping;
- Steel water tank interiors;
- Ductile or cast-iron pressurized piping under floor (slab on grade) in soil;
- Underground heat distribution and chilled water piping in ferrous metallic conduit in soils;
- Other structures with hazardous products

Protection by a Sacrificial Anode (SA) (Fig. 5.8 b)

- Pipelines buried underground are protected in this way
- Method relies on conductive pathways through the soil
- Spacing coating design and coupling are important factors

■ Anodes are fixed in bands weighing 300 to 400 kg at intervals of about 150 m

The reactions:

anode $Zn \mid Zn - 2e \rightarrow Zn^{2+}$ is oxidizing

cathode $Fe \mid O_2 + 2H_2O + 4e \rightarrow 4OH^-$

is protected

SA protective effect is estimated by following indexes.

- *Theoretic current efficiency* k_T which is calculated as:

$$k_T = \frac{zF}{M},$$

where z – a number of electrons in the SA oxidation,

M – SA metal molar mass, g/mol;

- *Experimental current efficiency* k_E:

$$k_T = \frac{It}{\Delta m_E},$$

where I – protective current at SA operating, A;

t – operating time, sec;

Δm_E – change in SA mass, g;

- *SA efficiency CE*:

$$CE = \frac{k^E}{k^T} \quad 100\%;$$

- *Protective affect Z*.

5.7 CONTROL TASKS

5.7.1 For the metal given in your variant of Table 5.2. determine:

- Factors accelerating corrosion;
- Metals for anodic and cathodic coatings, and complete reactions occurring in both cases in wet atmosphere (pH 7).

Table 5.2 – Test variants

#	Metal	Factor	#	Metal	Factor
1	Be	Alkalization Aeration Acidification	9	Ti	Anodization Na_2CO_3 treatment CO_2 bubbling
2	Al	Na_2CO_3 treatment Aeration Acidification	10	Ag	Acidification Cl^- addition Aeration
3	Co	Alkalization Acidification Deaeration	11	Mg	Alkalization Aeration Acidification
4	Cu	Alkalization Aeration Acidification	12	Zr	Anodization Alkalization CO_2 bubbling
5	Zn	Alkalization Chromate treatment Acidification	13	Bi	Alkalization Acidification Aeration
6	Fe	Deaeration Cu^{2+} addition CO_2 bubbling	14	Pb	Addition O_2 Acidification Cl^- addition
7	Ni	Alkalization Acidification Cl^- addition	15	Cd	CO_2 bubbling Aeration Acidification
8	Mn	Na_2CO_3 treatment Acidification Cl^- addition	16	Sn	Alkalization Acidification Deaeration

5.7.2. Determine the characteristic of SA (Table 5.3), applying for steel bank with drinking water protection. Complete the half-reaction of corrosion process at pH.

Table 5.3 – Test variants

#	SA material	Operating time *t*, day	SA mass *m*, kg	Protective current *I*, A	Z, %
1	Zn	365	?	3	95
2	Al	?	10	3.5	85
3	Mg	298	10	?	65
4	?	400	5	2.5	55
5	Zn	?	20	2.5	90
6	Al	329	40	?	82
7	Mg	342	?	3.5	70
8	?	402	10	3.2	86
9	Zn	305	20	?	93
10	Mg	?	20	1.5	68
11	Al	312	?	0.9	87
12	?	379	20	1.6	89
13	Zn	408	25	?	96
14	Al	?	10	0.6	84
15	Mg	374	?	2.2	70

5.8 EXPERIMENTAL PART

Experiment 1. Study of protective effect of inhibitors

In four cup pour 50 ml 25–30 ml of sodium chloride solution and add 2–3 drops of red blood salt $K_3[Fe(CN)_6]]$, which is the reagent ions of iron (2+) and creates a their presence intense blue color.

The first cup, add 2 ml of water, the second – 2 ml of potassium dichromate, the third – 2 ml of sodium carbonate, and the fourth – a pinch of hexamine. In all cups place cleaned with sandpaper steel samples. By watch 10–15 minutes, observe in which glass a blue color appeared.

Analyze the course of anodic and cathodic reactions on the surface of samples and explain the mechanism of corrosion of iron in a neutral environment. Why sodium chloride solution is commonly used instead of another salt as an environment for corrosion tests?

Experiment 2. Protection by sacrificial anode

In a glass with a solution of sodium chloride, which adds red blood salt, place steel sample circuited coupled with zinc sample. Is there a blue color solution? Drip near a steel plate drop phenolphthalein and watch pink color. Explain this phenomenon. Write the cathodic and anodic reactions corrosion process.

Experiment 3. Cathodic protection

In a glass with a solution of sodium chloride is added to the red blood salt, place the steel sample and connect it to the negative pole of DC power, carbon rod connects to the positive pole of the power source and shut the electric circuit. Is there a bluish solution? Close to steel sample drip phenolphthalein solution and watch the pink color. Explain the phenomenon observed.

Experiment 4. Study of the corrosion behavior of galvanized and tinned iron

In two glasses pour solution of sodium chloride and add a few drops of red blood salt. In one glass dip galvanized iron sample, and in the second – tinned one. Observe where blue color appears. Explain phenomena observed.

Protective potentials for metals in soil and water *vs* copper-sulfate reference electrode

Metal	Potential, V
Iron and Steel	–0.85
Lead	–(1.2–0.6)
Aluminum	–(1.2–0.9)
Copper	–0.2

Protective current density for steel

Environment	Густина струму, А/м^2
Soil	0.01 – 0.5
Fresh water	0.02 – 0.05
Sea water	0.05 – 0.15
Flowing sea water	0.15 – 0.30
Sulfuric acid (hot)	400

Scale of metals corrosion resistance

Group of stability	Corrosion index, mm/year	Resistance score
I. Very stable	<0.001	1
II. Enough stable	0.001...0.005	2
	0.005...0.01	3
	0.01...0.05	4
III. Stable	0.05...0.1	5
	0.1...0.5	6
IV. Lowered stability	0.5...1.0	7
	1.0...5.0	8
V. Low stable	5.0...10.0	9
VI. Non-stable	>10.0	10

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Редактор Т.М. Байрачна

План 2018 р., поз. 42
Підп. до друку 30.11.2018 р. Формат 60 х 84 1/16. Папір офсетн.
Друк офсетний. Гарнітура Times New Roman. Ум. друк. арк. 16,0.
Обл.-вид. арк. 19,0. Наклад 300 прим. 1 завод 40 прим.
Зам.№

Видавничий центр НТУ “ХПІ”
Свідоцтво про державну реєстрацію ДК № 3657 від 24.12.2009 р.
61002, Харків, вул. Фрунзе, 21

Друкарня