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## **CHEMISTRY**

Lecture synopsis for students  
of specialty 5B071800 – Electrical power engineering

Almaty 2016

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Lecture synopsis is worked out for bachelor students of specialty 5B071800 – Electrical power engineering, according to the educational standard for technical directions for rate "Chemistry" course.

Tables 2, References – 10.

Reviewer: Doct. Chem. Sci., G. Zh. Yelegbayeva, Prof. of KazNTU named after K.I. Satpayev.

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## **Introduction**

Lecture synopsis is worked out for bachelor students of specialty 5B071800 – Electrical power engineering, studying chemistry in volume of two credit. The course aim is to help students in preparation for examination, as well as for intermediate and current control in chemistry.

The contents of lecture synopsis correspond to the curriculum of the course of chemistry and consist of 8 lectures including the main sections of inorganic chemistry and electrochemistry.

Lectures are the most important part of chemistry course.

The lecture synopsis contains basic concepts and laws, formulas and reaction equations as well as mathematical calculations. When working at the lecture synopsis it is recommended to solve problems in chemistry, which will contribute to better understanding and consolidation of educational material.

## Introduction

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### **Lecture 1. Basic principles and laws of a chemistry. Classification of inorganic compounds**

Lecture content: basic concepts and laws of chemistry, classification of inorganic compounds.

Lecture objective: to introduce basic concepts of chemistry, to study main stoichiometric laws of chemistry and classes of inorganic compounds.

#### *Basic concepts of chemistry.*

Everything that surrounds us might be called with one common word which has a philosophic meaning - "the matter". Matter exhibits both wave-like and particle-like properties, the so-called wave–particle duality.

A substance consists of particles, which have their own rest mass of atoms, molecules and ions.

A wave is a form of existence of matter, which is mainly characterized by energy (for example, electromagnetic waves or gravitational ones).

The property of a matter is movement. The forms of movement are really various and linked with each other. One form can be turned into another (chemical movement can be transformed into thermal, thermal into electric, etc.).

So, *chemistry* is a branch of physical science that studies the composition, structure, properties and change of matter.

*The subject of chemistry:* Chemistry mainly deals with atoms and molecules, as well as their interactions and transformations.

A *chemical element* is a pure substance which is composed of a single type of atom, characterized by its particular number of protons in the nuclei of its atoms, known as the atomic number and represented by symbol  $Z$ .

An *atom* is the smallest particle of a chemical element having all its chemical properties.

A molecule is the smallest part of a substance called a compound that is that substance. Molecules are composed of atoms joined together chemically. Molecules do not have an electrical charge. If a molecule consists of a single type of atom, it is called a homoatomic molecule, and the substance is called pure chemical substance (for example O<sub>2</sub>, H<sub>2</sub>). A molecule which consists of different types of atoms forms a compound substance (CO, H<sub>2</sub>O, etc.).

*An amount of substance* is a number structural elements (atoms of, molecules, ions etc.) in a system. An amount of substance is measured in moles.

$$n = \frac{m}{M}, \text{ mole.}$$

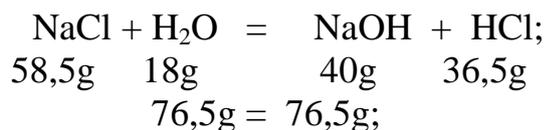
The mole is the unit of measurement in the International System of Units (SI) for amount of substance. It is defined as the amount of a chemical substance that contains as many elementary entities, e.g., atoms, molecules, ions, electrons, or photons, as there are atoms in 12 grams of carbon-12 (<sup>12</sup>C), the isotope of carbon with relative atomic mass 12 by definition. This number is expressed by the Avogadro constant, which has a value of 6.022140857(74) × 10<sup>23</sup> mol<sup>-1</sup>. The mole is one of the base units of the SI, and has the unit symbol mol. The mass of one mole of a substance is its molar mass

$$M = \frac{m}{n}, \text{ g/mole.}$$

Molar mass of substance equivalent is equal to M<sub>e</sub> = f<sub>e</sub> · M, where f<sub>e</sub> =  $\frac{1}{z}$  (z – basicity of a substance).

*Basic laws of chemistry:*

a) The most fundamental concept in chemistry is the law of mass *conservation*, which states that there is no detectable change in the quantity of matter during an ordinary chemical reaction.



b) *law of equivalents*: substances react with each other in a quantity which is proportional to their equivalents

$$\frac{m_A}{m_B} = \frac{\mathcal{E}_A}{\mathcal{E}_B}.$$

*An equivalent* is a unit of a substance which corresponds to one ion of hydrogen in a given acid-base reaction, or one electron in a given redox reaction. The factor of equivalence is used to determine an equivalent. It is a number which shows the proportion of a real unit of substance that corresponds to one ion of hydrogen in a given acid-base reaction, or one electron in a given reduction-oxidation reaction.

$$f_e = \frac{1}{z} \text{ (z – basicity of a substance).}$$

Basicity of a substance (z) equals:

1) for acids – the number of atoms of hydrogen in a given acid

$$f_e(\text{HNO}_3) = \frac{1}{1} = 1; \quad f_e(\text{H}_3\text{PO}_4) = \frac{1}{3};$$

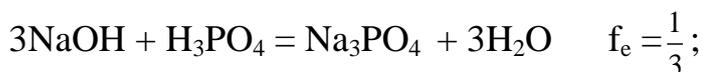
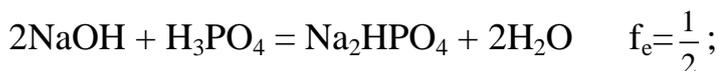
2) for bases – the number of hydroxides  $\text{OH}^-$  (or charge of a metal ion)

$$f_e(\text{NaOH}) = \frac{1}{1} = 1; \quad f_e(\text{Ca}(\text{OH})_2) = \frac{1}{2};$$

3) for salts and oxides – number of ions multiplied by a metal charge

$$f_e(\text{Na}_3\text{PO}_4) = \frac{1}{3}.$$

The factor of equivalence may be changed depending on a reaction:



c) *law of constant composition*, which states that all samples of a given chemical compound have the same elemental composition by mass.

For instance:  $M_r(\text{Na}_3\text{PO}_4) = 164$ ;

$M(\text{Na}_3\text{PO}_4) = 164 \text{ g/mole}$ .

In this composition, the sodium composes:

164 g/mole - 100 %

69 g/mole - x %

$x = 42,073 \%$ ;

phosphor: 164 g/mole - 100 %

31 g/mole - x %

$x = 18,902 \%$ ;

oxygen: 164 g/mole - 100 %

64 g/mole - x %

$x = 39,024 \%$ .

$$\sum Na + P + O = 100\% .$$

The chemical compound with constant compositions are called daltonides, and compounds with variable composition are called bertollides;

d) *law of multiple proportion*: if two elements form more than one compound between them, then the ratios of the masses of the second element which combine with a fixed mass of the first element will be ratios of small whole numbers.

For example, Dalton knew that the element carbon forms two oxides by combining with oxygen in different proportions. A fixed mass of carbon, say 100 grams, may react with 133 grams of oxygen to produce one oxide, or with 266 grams of oxygen to produce the other. The ratio of the masses of oxygen that can react with 100 grams of carbon is  $266:133 \approx 2:1$ , a ratio of small whole numbers. Dalton interpreted this result in his atomic theory by proposing (correctly

in this case) that the two oxides have one and two oxygen atoms respectively for each carbon atom. In modern notation the first is CO (carbon monoxide) and the second is CO<sub>2</sub> (carbon dioxide).

*e) Avogadro's law* states that, "equal volumes of all gases, at the same temperature and pressure, have the same number of molecules".

*So, we can say that:*

1) 1 mole of any substance consists of the same amount of molecules –  
N<sub>A</sub> = 6,022 · 10<sup>23</sup> (Avogadro's constant);

2) if moles of different gases in equal conditions have equal volumes, at a standard temperature and pressure, the molar volume is 22,414 liters/mol (p=101,325 kPa and T= 273,15 K);

3) the mass of different gases occupying equal volumes are proportional to each other as their molar mass.

$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \text{ if } V_1 = V_2.$$

*Classification of inorganic compounds.*

There are the following classes in inorganic chemistry: acids, salts, bases and oxides.

An acid is a chemical compound that consists of hydrogen ions and acid residual. Acids are divided into monobasic and polybasic acids (according to hydrogen ions), oxyacid and hydric acids.

Salts are chemical compounds which consist of metal ion and acid residual. Salts are classified by into neutral salts (Na<sub>2</sub>SO<sub>4</sub>), acid salts Ca(HCO<sub>3</sub>)<sub>2</sub> and basic salts (CuOH)<sub>2</sub>SO<sub>4</sub>.

Bases (hydroxides) are chemical compounds which consist of metal ions and hydroxyl functional group (OH<sup>-</sup>). They are classified into soluble bases (alkali) and insoluble bases, basic or amphoteric.

An oxide is a chemical compound that contains of at least one oxygen atom and one other element in its chemical formula. They are classified into salifiable and insalifiable oxides. Salifiable oxides are subdivided into basic, amphotermal or acid oxides.

## **Lecture 2. Atomic structure. Periodic law and Mendeleev's periodic table**

Lecture content: atomic structure, quantum numbers, Mendeleev's periodic table and its connection with the atomic structure.

Lecture objective: to study quantum mechanical model of atomic structure and its connection with Mendeleev's periodic table of elements.

*Structure of Atom: Quantum Mechanical Model. Quantum Numbers.*

In 1927, Heisenberg (Germany) postulated an uncertainty principle. The uncertainty principle says that it is impossible to identify the location and the momentum of an electron in an atom, at any one time, with absolute precision. At

any moment of time it is possible to determine only one of those properties. In 1926 E. Schrödinger (Austria) defined the mathematical description of electron's behavior in an atom.

The works of Planck, Einstein, Bohr, de Broil, Heisenberg and also Schrodinger established fundamentals of quantum mechanics, which studies the movement and interaction of micro particles.

*Orbital.* According to quantum mechanics it is impossible to define precisely the energy and position of electron, i.e. to characterize the position of an electron in quantum mechanical model of an atom we use a probability approach. The probability of electron location in a particular area of space is described by wave function  $\varphi$ , which characterizes wave amplitude as function of electron's coordinates. In the most common situation this function depends on three dimensional coordinates, and it is called an orbital. According to  $\forall$  definition, orbital is a physical region or space where an electron is supposed to be present. Such a region of space is called an orbital. An orbital is limited by surfaces of three-dimensional area.

The orbital of electron that has a negative charge has a defined configuration, therefore its orbital is called an electron cloud.

*Quantum numbers* are used in order to characterize the behavior of electron in an atom. They can be principal quantum number (n), azimuthal quantum number (l), magnetic quantum number (ml), and spin quantum number (ms).

The principal quantum number (n) defines the energy level and sizes of electronic orbitals. It takes simple numbers as 1, 2, 3, 4, 5, ... and describes the electron shell, or energy level of an atom. The bigger n is the higher energy level of electron is. Shells (levels) have their letters: K (n=1), L (n=2), M (n=3), N (n=4), Q (n=5).

The azimuthal (orbital) quantum number (l) specifies the shape of an atomic orbital. Electronic shells are divided into subshells, that's why the azimuthal quantum number also characterizes energy sublevels in electronic shell of an atom. The azimuthal quantum numbers have values from 0 to (n-1). Subshells are indicated by letters

	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
The azimuthal quantum number . . .	0	1	2	3

Electrons, azimuthal quantum number of which is 0, are called s-electrons. Orbitals and electronic clouds are spherical.

Electrons, azimuthal quantum number of which is 1, are called p-electrons. Orbitals and electronic clouds look like a dumbbell.

Electrons, azimuthal quantum number of which is 2, are called d-electrons. The orbitals have more complex shape than p-orbitals.

Electrons, azimuthal quantum number of which is 3, are called f-electrons. The shape of its orbitals are even more complex than d-orbitals.

In the same shell (level) the energy of subshells (sublevels) grows in a row:

$$E_s < E_p < E_d < E_f.$$

In the first shell ( $n=1$ ) there can be one subshell ( $s$ -), in the second ( $n=2$ ) - two subshells ( $s$ -,  $p$ -), in the third ( $n=3$ ) - three ( $s$ -,  $p$ -,  $d$ ), in the fourth ( $n=4$ ) — four ( $s$ -,  $p$ -,  $d$ -,  $f$ -) subshells.

The magnetic quantum number ( $m_l$ ) defines the orientation of an orbital in space. The magnetic quantum number has values from  $-l$  to  $+l$  including 0.

Table 1 – Quantum numbers

n	l	$m_l$	$m_s$
f d p s	3 2 1 0	-3,-2,-1,0,1,2,3	-
d p s	2 1 0	-2,-1,0,1,2,	-
p s	1 0	-1,0,1	-
s	0	0	-

Spin quantum number ( $m_s$ ) specifies the own rotational movement of electron around its own axis, or shows the value and orientation of spin. It has only two values  $+1/2$  and  $-1/2$ .

To sum up, the condition of an electron in an atom is fully characterized by four quantum numbers:  $n$ ,  $l$ ,  $m_l$ ,  $m_s$ .

Paulis principle, Hund's and Klechkovski's rules.

*Paulis principle*: it is impossible for two electrons of a poly-electron atom to have the same values of the four quantum numbers.

The distribution of electrons over levels and sublevels are described by electronic formulas and energy cells.

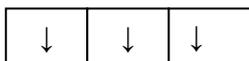
For example, electronic formula of hydrogen is  $1s^1$

helium is  $1s^2$

lithium is  $1s^2 2s^1$

carbon is  $1s^2 2s^2 2p^2$ .

*Hund's rule* states that summary spin quantum number of electrons has to be maximum, i.e. orbitals of a given sublevel are filled by one electron, then by the second one. For example, the following distribution of electrons corresponds to stable state of an atom.



Klechkovski's Rule:

1) Filling of orbitals occurs from  $n+l$  smaller to  $n+l$  greater. For example,

4s    3d

$4+0 < 3+2$  (4s is filled first, then 3d).

2) If the sums of  $n+l$  are equal to each other filling of orbitals is made in a growing order of number  $n$ . For example,

4p    3d

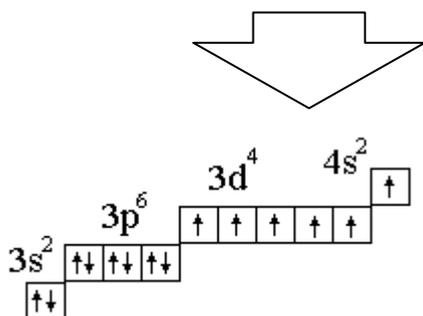
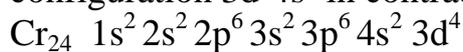
$4+1 = 3+2 \Rightarrow$  firstly 3d is filled, then 4p.

According to Klechkovskis Rule, the subshells line up in a row:

$1s < 2s < 3s < 4s = 3d < 4p < 5s = 4d < 5p < 6s = 5d = 4f < 6p < 7s$  and so on.

There are some exceptions from this rule (Cu, Ag, Cr, Mo, Pd, Pt).

For example, chromium has only one electron on 4s subshell, but on 3d-subshell it has 5 d-electrons instead of 4. This occurs because of low energy configuration  $3d^5 4s^1$  in contradiction to configuration  $3d^4 4s^2$ .



*Mendeleev's periodic law, and its connection with atomic structure.*

Properties of simple substances as well as shape and properties of complex elements have a periodic dependence on atomic masses of these elements. Periodic system is a graphical representation of the periodic law.

Modern explanation of the periodic law is that the properties of elements and their bounds are in a periodic dependence on charges of their nuclei.

As electronic structure of elements changes periodically, so do the properties of elements that are defined by their electronic structure:

a) ionization energy (IE) of an atom or molecule describes the minimum amount of energy required to remove an electron (to infinity) from the atom or molecule. It is measured by kJ/mol, or electronvolts (eV). Alkaline metals have the least values of ionization energy;

b) electron affinity of an atom or molecule is as the amount of energy released when an electron is added to a neutral atom or molecule to form a negative ion. Halogens and oxygen have the greatest measures of electron affinity;

c) electronegativity is the ability of atoms to attract electrons. The greater the electronegativity is, the easier an atom is turned into a charged ion. Electronegativity of elements: Li = 1; Na = 0,9; K = 0,8; Cs = 0,7; Be = 1,5; Mg = 1,2; B = 2; P = 2,5; F = 4.

### **Lecture 3. Chemical bond**

Lecture Content: types of chemical bonds, hybridization of atomic orbitals (AO), method of bond valence (BV), and method of molecular orbitals (MO).

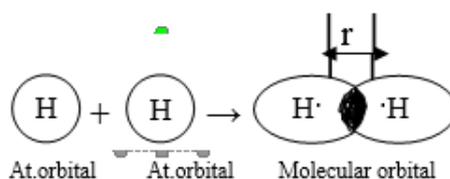
Lecture objective: to study types of chemical bonds and their difference, to study origin of hybrid orbitals and their variety.

*Chemical bond* is combination of forces operating between atoms or groups of atoms. The conditions of appearance of chemical bond are contact of interactive atoms and merging their electronic shells.

We can distinguish three types of chemical bonds: covalent, ionic and metallic.

*Covalent bond* is a common type of bonding, in which the electronegativity difference between bonded atoms is small or does not exist.

Formation of covalent bonding can be evident in the reaction of hydrogen atoms resulting in the formation of a molecule of hydrogen. When hydrogen atoms react, electronic density in the area of merging clouds increases, attractive power between atoms increases to, but the energy of the system decreases, and thus bonding:  $H \cdot + \cdot H \rightarrow H:H$  appears



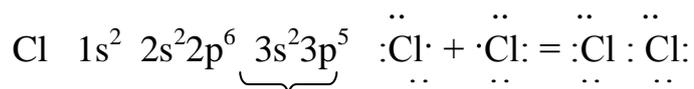
Picture 3.1 – Formation of chemical bond in a hydrogen molecule

Interactive electrons must possess antiparallel spins.

The distance between atoms of hydrogen and energy of bond were calculated in 1927:  $r_{H-H} = 0,074$  nm,  $E_{H-H} = 436,2$  kJ/mole.

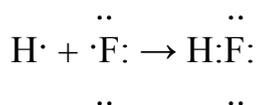
Covalent bond can be polar and non-polar.

Non-polar covalent bond exists in molecules, where every nucleus is an atom attracts a pair of bonding electrons with equal force. For example,  $H_2$ ,  $Cl_2$ ,  $O_2$  etc.



Polar covalent bond exists in  $n \cdot 7\bar{e}$  les, where a pair of electrons forming chemical bonding is displaced to one of nuclei of atoms.

Interactive atoms are characterized by different electronegativity (for example,  $H_2O$ ,  $H_2S$ ,  $CO_2$ ,  $NH_3$  etc.). In HF molecule, a common pair of electrons is displaced toward a fluorine, because electronegativity of fluorine is bigger than electronegativity of hydrogen.

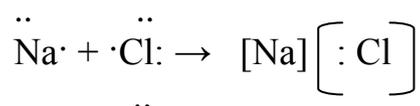
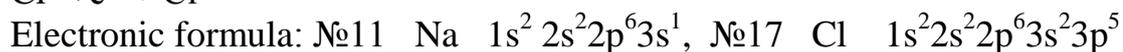
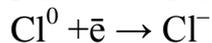
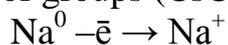


Covalent bond has the following features:

a) saturability: only external shell electrons participate in a chemical reaction, thus there is a limited number of electrons;

b) directivity: an area of merging of electronic clouds is in certain direction in relation to interactive atoms.

*Ionic bond* is chemical bonding between ions, carried out by electrostatic attraction. This type of bonding appears only in the case of large difference of electronegativity of atoms, for example, between cations of s - metals of the first and second groups of the periodic system and anions of non-metals of the VIth and VIIth of groups (CsCl, K<sub>2</sub>O, LiF, and others). For example,



*Metallic bond.* In this type of bonding, each atom in a metal gives one or more electrons to a "sea" of electrons that reside between many metal atoms. In this sea, each electron can be associated with great many atoms at once. Nature of the connection is electric.

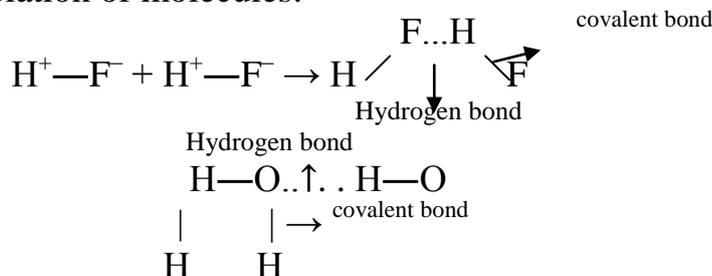
Because of low ionization energy the electrons in a metal lose bonding with separate atoms, easily become freely associated with many atoms at once, forming electronic gas – a set of "free" electrons. Electrons in a metal are movable, i.e. delocalized.

Within covalent bonding, valence electrons of only two nearby atoms can be freely associated with many atoms, while within metallic bonding all atoms take part in association of these electrons.

*Hydrogen bond* can be intermolecular and intramolecular.

Intermolecular hydrogen connection arises up between molecules, which have hydrogen and such electronegative elements as a fluorine, oxygen, nitrogen, rarely chlorine and sulphur.

In such a molecule a common electronic pair is displaced from hydrogen to an atom of electronegative element, but its positive charge is concentrated in a small volume. Proton reacts with an undivided electronic pair of another atom or ion, generalizing it. As a result, the second weaker bond appears with the help of hydrogen. Features of these bonds are directivity and saturability. Hydrogen bond is responsible for the association of molecules:



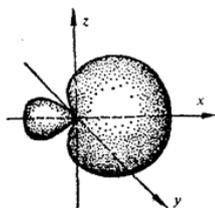
*Hybridization of atomic orbitals.* There are four connections of C-H in the molecule of CH<sub>4</sub>-methane, which have equal lengths and energy. Meanwhile, a carbon in an excited state has three p- and one s- orbitals with the uncoupled

electrons that are merged by the s- orbitals of hydrogen. On this basis, it was possible to expect that characteristics of one bond in a molecule of methane will differ from characteristics of other bonds. All four bonds in the molecule of methane are equivalent.

If an atom which enters into chemical bond has different AO (s -, p-, d - or f-AO), hybridization of AO appears in the process of chemical bond formation. Thus identical (equivalent) AO appears from different AO. It is necessary to emphasize that hybrid of AOs appears within one atom having different orbitals. Thus, hybridization takes place at orbitals that have close values of energy.

The form of hybrid AO differs from the form of initial AO. In hybrid AO the electronic density is displaced to one side from a nucleus, therefore within an interaction with AO of an other atom maximal merging area appears that results in the increase of bond's energy. This increase of energy compensates the energy required to form hybrid orbitals. Chemical bonds formed by hybrid orbitals are stronger, and a molecule is more steady.

a)  $sp$  - hybridization:  $1s + 1p$  orbitals



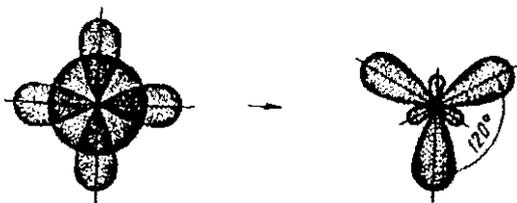
Picture 3.2

b)  $sp^2$  - hybridization:  $1s + 2p$  orbitals



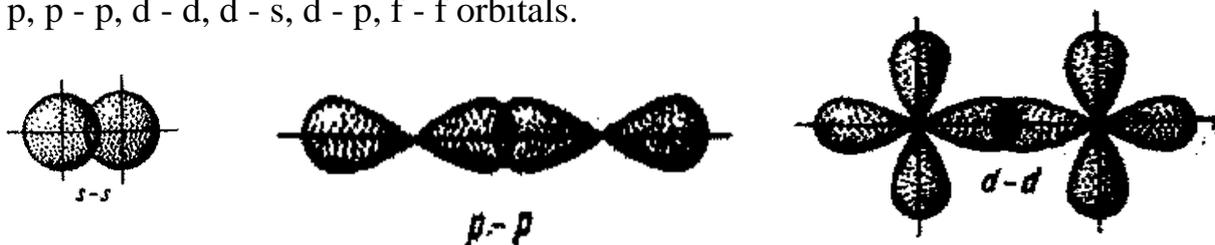
Picture 3.3

c)  $sp^3$  - hybridization:  $1s + 3p$  orbitals



Picture 3.4

$\sigma$ -connection is the connection defined by merging atomic orbitals on a line, connecting the nuclei of interactive atoms. Sigma-bond can arise at merging: s - s, s - p, p - p, d - d, d - s, d - p, f - f orbitals.



Picture 3.5

$\pi$ -connection is the connection, formed by merging AO on both sides of the line, connecting the nuclei of atoms (lateral merging), : p - p, p- d, d - d, f - p, f - d, f - f.



Picture 3.5

When  $\pi$ - is imposed on  $\sigma$ -bond, a double bond appears, for example, in molecules of oxygen, ethylene and carbon dioxide.

When two  $\pi$ - bonds are imposed on  $\sigma$ -bond, triple connection appears, for example, in molecules of nitrogen, acetylene and carbon oxide.

In a molecule of nitrogen of  $N\equiv N$ . There is one  $\sigma$ -bond ( $p_x - p_x$ ), and two  $\pi$ -bonds ( $p_y - p_y$  and  $p_z - p_z$ ).

The mechanism of covalent bond appearance was considered at the example of formation of hydrogen of a molecule. Further, V.Heitler and F.Pauling spread these ideas on polyatomic molecules and offered the method valence bond (VB). The method of molecular orbitals (MO), mainly developed by of Mulliken and Hund works is successfully used along with valence bond method.

Method of VB is based on the following general rules:

- chemical bond between two atoms occurs and it results from merging AO with the formation of electron pairs (sharing two electrons);
- atoms entering into chemical bond exchange electrons that form electron-pair bond. Energy of electron exchange between atoms (attraction energy of atoms) makes a basic contribution to energy of the chemical bond. An additional contribution to the bond energy is made by coulomb forces of interactive particles;
- in accordance with Pauli's principle, a chemical bond appears only when electrons interact with antiparallel spins;
- characteristics of chemical bond (energy, length, polarity and others) are determined by the type of merging of AO.

According to VB theory, covalent bond is directed toward maximal merging AO of reactive atoms.

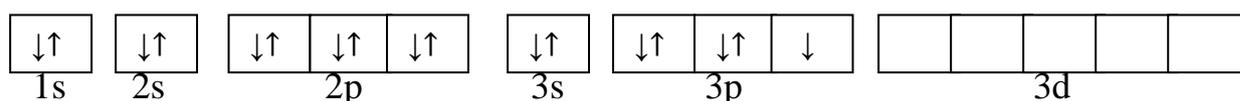
*Valence by the exchange mechanism of VB method.* The ability of atom to attract or substitute a certain number of other atoms while forming chemical bonds is called *valency*. According to the exchange mechanism of VB method, every atom gives one unpaired electron to form a general electronic pair (of covalent bond).

The number of unpaired electrons in an atom in stable or excited state is considered as quantitative measure of valence in exchange mechanism of VB method.

While forming a chemical bond, an atom can pass to an excited state because of disconnection of a pair (or pairs) of electrons, and passage of one electron (or a few electrons, equal to the number of disconnected pairs) to a free orbital of the same shell.

For example, let's consider an atom of chlorine :

№17 Cl electronic formula -  $1s^2 2s^2 2p^6 3s^2 3p^5$



Picture 3.6- Graphic formula

In unexcited state, the amount of unpaired electrons is equal to unit, therefore valency  $V = 1$ . In excited state, there is unpairing of electrons on  $3s$  -,  $3p$  - sublevels and they can place themselves on the free orbitals of  $3d$ -sub-level. Valence of chlorine in excited state can be equal to  $V = 3, 5, 7$ .

*Method of molecular orbitals.* According to MO method, electrons in molecules are distributed on molecular orbitals that are characterized by certain energy (by a power level) and form like atomic orbitals (AO). Unlike AO, molecular orbitals are able to embrace not only one atom, but the whole molecule, and thus they are two- or multicentral. If in VB method the atoms of molecules keep a certain individuality, in MO method a molecule is examined as a single system.

#### Lecture 4. Chemical kinetics

Lecture content: speed of chemical reactions and factors influencing on them; chemical equilibrium and Le Chatelier's principle.

Lecture objectives: to know basic concepts of chemical kinetics, to consider the influence of different factors on the speed and direction of a chemical reaction.

Chemical kinetics studies of the speed and the mechanism of chemical reactions.

The speed of a reaction is the change of a substance amount at a unit of time represented in a unit of volume (for a homogeneous reaction) or in a unit of surface area (for a heterogeneous reaction).

Homogeneous reaction is a reaction that occurs in a single phase e.g. (gaseous, liquid or solid).

Heterogeneous reaction is a reaction that occurs on the border of division of different phases (e.g. solid and liquid).

The second definition: The speed of a reaction is the change of concentration of reagents in a unit of time.

For homogeneous reaction:

$$v_m = \pm \frac{\Delta C}{\Delta t} = \pm \frac{(C_2 - C_1)}{t_2 - t_1}.$$

Example:  $N_2 + 3H_2 = 2NH_3$ ,

$$v = -\frac{dC(N_2)}{dt} = -\frac{dC(H_2)}{3dt} = +\frac{dC(NH_3)}{2dt}.$$

The speed of a reaction is measured in: mole/l·c, mole·sm<sup>-3</sup>·c<sup>-1</sup>.

For heterogeneous reaction:

$$v_m = \pm \frac{\Delta C_s}{\Delta t}, \quad v_{instant} = \pm \frac{dC_s}{dt}.$$

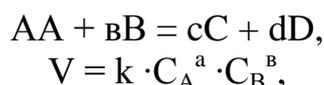
For example  $Si_{(K)} + O_2 = SiO_{2(K)}$ .

The speed of a reaction at a constant temperature is  $v = k \cdot C_{O_2} \cdot S$ , where S is the surface of division between phases.

The speed of a reaction cannot be negative, because the concentration and time cannot be negative. The sign (-) means that the speed of reaction is calculated by decreasing the concentration of reagents.

The speed of reaction depends on the nature of reagents, concentration, temperature, the appearance of catalyst.

The dependence of reaction speed of on concentration of reagents is expressed by *Guldberg-Waages law of mass action*: the rate of elementary chemical reaction is proportional to the product of the concentrations of the reactants in a degree equal to the stoichiometric coefficients in the reaction equation



where  $k$  is the rate constant of the reaction. Physical sense of  $k$  is that it is numerically equal to the speed of chemical reaction, if the concentration of reagents equals 1 mol/liter.  $k$  depends on the temperature and appearance of a catalyst, as well as it does not depend on concentration.

*Exponent* (a and b) in a concentration in the given equation is called the order of the reaction in a given substance.

The total kinetic reaction order of reaction  $n = \sum n_i$ ,  $n_i$  - the order of reaction with respect to the  $i$ -th reagent.

The order of a reaction is a formal value, it can be positive or negative; as well as whole, fractional or equal to zero.

a) if  $n = 0$ ,

$$v = -\frac{dC}{dt} = k_0,$$

b) if  $n = 1$ ,

$$v = -\frac{dC}{dt} = k_1 \cdot C,$$

В) if n=2,

$$v = -\frac{dC}{dt} = k_2 \cdot C^2,$$

Г) if n=3,

$$v = -\frac{dC}{dt} = k_3 \cdot C^3.$$

The order of a reaction is usually defined experimentally.

*Molecularity* in chemistry is the number of molecules that come together to react in an elementary reaction:

$I_2 = 2I$  is unimolecular reaction (rearrangement of a single molecule);

$I_2 + H_2 = 2HI$  is bimolecular reaction;

$2NO + H_2 = N_2O + H_2O$  is trimolecular reaction, very rare.

For complex multiphase reactions the molecularity has no sense, because this concept is applicable only to elementary reactions.

*Van't Hoff's Rule*: When the temperature rises at a constant 10 degrees every elementary homogeneous reaction rate increased at two to four times.

$$\gamma = v_{T_2} / v_{T_1} \text{ at } T_2 - T_1 = 10 \text{ K,}$$

where  $v_{T_1}, v_{T_2}$  – rates of reaction at temperatures  $T_1$  and  $T_2$ .

$$k_{T_2} = k_{T_1} \cdot \gamma^{\frac{T_2 - T_1}{10}}.$$

At concentration of reagents 1 mole/liter  $v=k$ .

In 1889 Swedish scientist Arrhenius set the functional dependence of rate constant of chemical reaction  $k$  on the temperature.

$$k = A \cdot e^{\frac{-E_a}{R \cdot T}},$$

where  $A$  is a pre-exponential factor, which constitutes the entire frequency of collisions between molecules of reagents;  $E_a$  – energy of activation;  $e^{\frac{-E_a}{R \cdot T}}$  – the proportion of molecules, which has extra energy of a activation  $E_a$  compared to medium energy of a activation of a molecule.

Solving the logarithm, we get

$$\ln k = \ln A - E_a / R \cdot T.$$

This equation allows us to calculate the energy of activation of the reaction.

From the equation it follows that the dependency of rate constant of a reaction  $\ln k$  in temperature made drawn in  $\lg k = -1/T$  coordinates is linear to  $\text{tg } \alpha = E_a / 2,3 \cdot R \cdot T$ .

This dependency allows us to define activation energy of  $E_a$  using tangent of

$$\ln \frac{k_2}{k_1} = \frac{-E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right), \quad \ln \frac{v_2}{v_1} = \frac{-E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

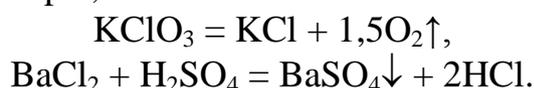
an a slope angle of a straight line and pre-exponential factor A along the segment of y- axis, when  $1/T=0$ .

*Activation energy* is some extra amount of inner energy (in comparison with medium one), which molecule should have in order to react in a given chemical reaction.

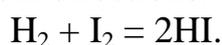
Activation energy is needed to overcome repulsive forces between approaching molecules, weaken and break bonds in molecules of reactants. The greater the value of activation energy is, the smaller the speed of reaction and vice versa.

Chemical reactions are divided into reversible and irreversible ones.

Irreversible - reactions are reactions in which at least one of the reactants is completely consumed, and the product of the reaction can be precipitate, gas or insoluble substance. For example,



Reversible reactions occur in both directions:



First, the direct reaction goes at high speed  $V_1 = k \cdot C_{\text{H}_2} \cdot C_{\text{I}_2}$ . While accumulating HI the counter reaction occurs at higher speed:  $V_2 = k \cdot [\text{HI}]^2$ . After some period of time the speed of direct and occurs reaction equalize and *chemical equilibrium* occurs/ It is the state of a system of reactants, when the speeds of opposite reactions are equal.

The concentration of reactants which are set in a chemical equilibrium are called equilibrium concentrations.

Usually the equilibrium concentrations are marked with squared brackets  $[\text{I}_2]$ ,  $[\text{H}_2]$  in contrast to unequal concentration  $C_{\text{H}_2}$ ,  $C_{\text{I}_2}$ ,  $C_{\text{HI}}$ .

Concentration of reactants, temperature, pressure (for gases) have an influence on the state of chemical equilibrium.

Let's express the speed of direct and couter reaction according to the law of acting masses.

$$v_1 = k_1 \cdot [\text{H}_2] \cdot [\text{I}_2], v_2 = k_2 \cdot [\text{HI}]^2.$$

At equilibrium the speed of direct reaction equals to the speed of couter one  $V_1=V_2$ , and then  $k_1 \cdot [\text{H}_2] \cdot [\text{I}_2] = k_2 \cdot [\text{HI}]^2$ . Let's rearrange the equation.

$$K = \frac{k_1}{k_2} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]},$$

where K - constant of chemical equilibrium.

$k_1, k_2$  are constant at the same temperature, and their ratio is also constant.

The constant of equilibrium is depends on temperature and the nature of reactants, but it does not depend on their concentration. The constant of equilibrium shows how much the speed of direct reaction exceeds the speed of a counter reaction, if the concentration of each of reactants equals 1 mol/l. That's the physical meaning of  $K_{eq}$ .

Chemical equilibrium is the most stable state of a system under given conditions. When conditions change, the equilibrium is disturbed and shifted to the left or right.

The direction of displacement is determined by *Le Chatelier's principle*: if external factors affect on a system that is in equilibrium, the equilibrium is shifted in the direction that reduces the effect of external influences. The change in temperature, concentration and pressure affect on the shift of equilibrium.

For endothermic reaction: when temperature increases, the equilibrium is shifted to the right, because a direct reaction proceeds with heat absorption  $\Delta H > 0$ . For exothermic reaction ( $\Delta H < 0$ ) when temperature rises, the equilibrium shifts to the left, when temperature falls - to the right.

Let's look at the shift of the equilibrium of a system:



The concentration of one of the initial materials being increased, the equilibrium shifts to the right side; and when the concentration of  $\text{NH}_3$  rises the equilibrium shifts to the left side, i.e. to the direction of decreasing concentration.

If at least one gaseous substance participates in a reversible reaction, the pressure affects on equilibrium.

With increasing pressure and constant temperature, the volume of gas is compressed, thus its concentration increases, and hence the speed of the reaction increases, so that the equilibrium is shifted towards the reduction of concentration of a gaseous component. To determine the direction of displacement of equilibrium it is necessary to count the number of molecules in the left and right sides of the equation. For the reaction of ammonia: in the left side the number of molecules is 4, in the right side is 2. The increase of pressure results in the decrease of the number of molecules, so that the equilibrium is shifted to the right. Reducing the pressure will shift the equilibrium to the left.

## **Lecture 5. The energy of chemical processes. Chemical thermodynamics**

Lecture content: the first and second laws of thermodynamics; the enthalpy and entropy; Gibb's free energy of reactions; Hess's law and consequences from it.

Lecture objectives: to calculate energy effects of chemical reactions, predict possibility and direction of reaction processes.

*Chemical thermodynamics* is a part of thermodynamics studying physical changes of chemical energy to other types of energy (electric, thermal, mechanical etc.) within the confines of the laws of thermodynamics

A thermodynamic system is any object of nature that consists of a large number of molecules (structural units) and separated from other objects of nature by the real or imaginary border of division.

Objects that are not included into a system are called a medium.

Systems are divided into:

a) isolated system: there is no exchange of the mass and the energy between the system and medium (The Universe, ice in an ideal thermos);

b) closed system: there is no mass-transfer between the system and medium, but there is an exchange of energy (the planet Earth, stone that is cooling off);

c) opened system: there is an exchange of mass and energy between the system and medium (man).

Systems are also divided into:

a) homogeneous system: consisting of one phase (air, NaCl in water);

b) heterogeneous system: consisting of two or a few phases (water with ice, solution with sediment).

A *phase* is a part of a system, separated from other its parts by dividing surface and the transition of that area sharply changes the properties of the system.

The state of a system is characterized by thermodynamical parameters: temperature (T), pressure (p), volume (V), internal energy (U), enthalpy (H), entropy (S), etc.

Parameters are subdivided into intensive and extensive.

Intensive parameters are such parameters the size of which does not depend on the size of a system (T, p, C,  $\tau$ ,  $\rho$ ).

Extensive parameters are such parameters the size of which depends on the sizes of a system (V, m, S, U, H, G). These measures increase proportionally the mass of the system.

*Internal energy* is a complete reserve of energy of a system, conditioned by kinetic and potential energies of particles.

Kinetic energy is the energy of translational, vibrational and rotational motions of particles.

Potential energy is the energy conditioned by attractive and repulsive forces between particles.

Internal energy is a thermodynamical function of the state of a system.

Function of the state of a system is such a function the change of which depends only on the initial and final state of the system and does not depend on the way in which the system acquired that state. As for the function of the state it is enough to define its change only.

The system transferring from initial state  $U_1$  to final state  $U_2$  accomplishes work [A], and there is some heat Q absorbed from the medium.

$$U_2 - U_1 = \Delta U = Q - A \Rightarrow Q = \Delta U + A = \Delta U + p\Delta V. \quad (1)$$

Equation (1) is a mathematical expression of law of energy conservation (the beginning of thermodynamics). The law was discovered by Joule in 1842, and it states that "energy is neither created nor destroyed, but it is only transformed from one kind of energy to another in strictly equivalent amounts".

If a chemical reaction flows at  $V = \text{const}$  or  $V = 0$  (isochoric process), the work of expansion of the system  $A = p\Delta V = 0$  and then  $\Delta U = Q_v$ , where  $Q_v$  is a thermal effect of chemical reaction or the amount of heat absorbed by the system at  $V = \text{const}$ .

Most chemical reactions flow at  $p = \text{const}$  or  $\Delta p = 0$  (isobar process). In these terms we use enthalpy measure to describe the process, not internal energy  $U$ .

Enthalpy  $[H]$  is the amount of heat content used or released in a system determined by the sum of internal energy and accomplished work measures.

$$Q_p = \Delta U + p\Delta V = (U_2 - U_1) + p(V_2 - V_1) = (U_2 + pV_2) - (U_1 + pV_1),$$

$$(U + pV) = H, \quad (2)$$

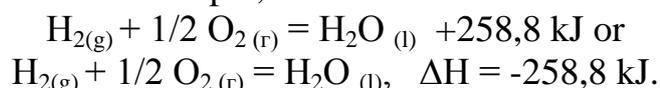
where  $H$  is enthalpy, function of the state of the system (depends only on the initial and final state of the system).

*Enthalpy of chemical reactions.*

The sum of released energy during a chemical reaction and all work accomplished by a reactive system in the medium, except the work of expansion, is called the *thermal effect of a chemical reaction*. Often the thermal effect of reaction is called the enthalpy of reaction.

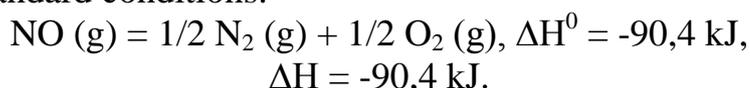
If the thermal effect of a reaction is positive, the reaction is called exothermic, if it is negative, the reaction is called endothermic.

The equations of reactions, taking into account thermal effects, are called thermochemical equations. For example,

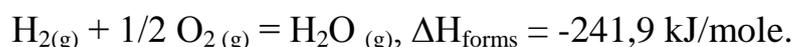


Let's consider thermal effects of different chemical processes.

*The enthalpy of a decomposition reaction* is the amount of energy per mole either released or produced at the decomposition of a compound substance into a simple one under standard conditions.



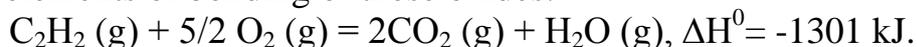
*The enthalpy of bond formation* is the amount of energy per mole either released or produced while forming a compound substance from simple ones under standard conditions.



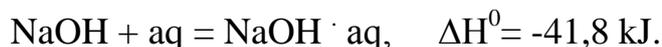
Standard conditions:  $p = 1 \text{ atm} = 101325 \text{ Pa}$ ,  $T = 298,15 \text{ K}$  ( $25^\circ\text{C}$ ).

The thermal effect measured in ordinary conditions is called the standard enthalpy of formation (decompositions) and it is designated as  $\Delta H_{298}^0$  or  $\Delta H^0$ . The heat of formation of simple substances is equal to zero.

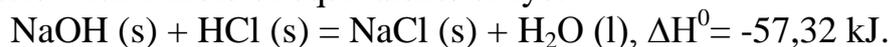
*The enthalpy of combustion* is a thermal effect of a reaction of oxidization of one mole of a given compound by oxygen while forming higher oxides of corresponding elements or bonding of these oxides.



*The enthalpy of dissolution* is a thermal effect of dissolution of 1 mole of a substance.



*The enthalpy of neutralization* is a thermal effect of reaction of 1 mole of equivalents of acid with 1 mole of equivalents of lye.

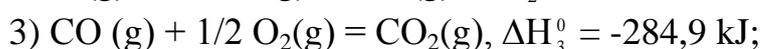


*The Hess's Law and consequences from it.*

In 1936 Hess stated that the thermal effect of a chemical reaction does not depend on intermediate stages, and is determined only by the final and initial state of the reactive system.

This postulate is considered as basic law of thermochemistry and it is called Hess's law.

Later it was discovered that this law is valid only for processes flowing when volume and pressure are permanent.

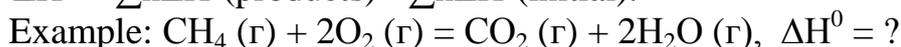


$$\Delta H_1^0 = \Delta H_2^0 + \Delta H_3^0.$$

Consequences from Hess's law :

1) The thermal effect of reaction is equal to the sum of heat of products formation except the sum of heat of initial substances formation.

$$\Delta H^0 = \sum n\Delta H^0(\text{products}) - \sum n\Delta H^0(\text{initial}). \quad (3)$$



To solve the problem we write out tabular data of heat of formation of all substances participating in the reaction from the reference book.

$$\Delta H^0 (\text{CO}_2) = -393,6 \text{ kJ/mole,}$$

$$\Delta H^0 (\text{H}_2\text{O}) = -242,0 \text{ kJ/mole,}$$

$$\Delta H^0 (\text{CH}_4) = -75,5 \text{ kJ/mole,}$$

$$\Delta H^0 (\text{O}_2) = 0 \text{ kJ/mole,}$$

$$\Delta H^0 = [-393,6 + 2(-242,2)] - [(-75,5) + 0] = -802,1 \text{ kJ.}$$

2. The heat of decomposition of a compound is equal to the heat of its formation in absolute value, but with an opposite sign.

$$\Delta H_{\text{dec}} = -\Delta H_{\text{for}}$$



*Entropy. The second beginning of thermodynamics.*

The first law of thermodynamics allows to calculate released heat, accomplished work, but it is unable to forecast the possibility of flowing process.

Some physical and chemical phenomena, and also chemical reactions are such processes that flow without any external exertions and they can be a source of work against external forces. For example, crystallization of super cooled liquids and saturated solutions, reaction of neutralization and formation of hard soluble electrolytes, combustion of organic products etc.

All these processes are irreversible that means that they do not allow the system to return to the initial state without any changes in an environment or in the system.

Possibility and direction of spontaneously a leak (irreversible) processes are stated by the second beginning of thermodynamics.

$$\Delta S \geq q/T, \quad (4)$$

where S is an entropy, quantitative measure of disorder, function of the state of the system; q - is an amount of heat, absorbed by the system; T is an absolute temperature.

The equality sign refers to reversible processes and the sign of inequality to irreversible ones.

Thus, in isolated systems processes flow spontaneously only if the entropy of the system increases. If in an isolated system only convertible processes are accomplished, the entropy of the system stays permanent.

#### *Gibbs's free energy*

Gibbs's free energy is a criterion of spontaneous flowing of process.

Processes flow spontaneously due to 2 factors:

- a) tendency of a system to the achievement of the minimum of energy (enthalpy factor  $\Delta$ of H);
- b) tendency of a system to the most well-organized and probable state (entropy factor of  $T\Delta S$ ).

The difference between enthalpy and entropy factors:  $\Delta G = \Delta H - T\Delta S$ . It allows us to judge about the possibility of spontaneous flow of a chemical process in this direction. If  $\Delta G < 0$ , the process flows spontaneously. If  $\Delta G > 0$ , the process will not flow spontaneously in this direction. The value of  $G = H - TS$  is called Gibbs's free energy.

## **Lecture 6. Solutions**

Lecture content: classification of solutions, strong and weak electrolytes, the constant and degree of electrolytic dissociation, activity and ionic strength of solutions, ph-scale, hydrolysis of salts, methods of defining solutions concentration.

Lecture objectives: to study classification of solutions, to conduct calculations in solutions of weak and strong electrolytes.

A homogeneous mixture with variable composition is called a *solution*. Substances that compose a solution are called components.

A solvent is a substance that does not change its aggregate state at dissolution and its concentration is higher than the concentration of other components.

A solute is a substance being in a solution in a smaller amount.

According to an aggregate state, solutions are divided into gaseous, liquid and solid ones. Liquid solutions are subdivided into aqueous and non-aqueous; solutions of electrolytes and those of non-electrolytes.

*The degree and constant of electrolytic dissociation.*

Dissociation of molecules of electrolytes to ions in solvents is called electrolytic dissociation.

Electrolytes are substances that dissociate in aqueous solutions into ions (salts, acids, bases, ampholytes). The conductivity of electrolyte solutions is higher than that of a solvent.

Non-electrolytes are substances that practically do not dissociate in aqueous solutions into ions (saccharide, glucose, urea etc.). The conductivity of non-electrolyte solutions almost does not differ from the conductivity of a solvent.

For the quantitative estimation of dissociation process we use the concept of the degree of dissociation. The degree of dissociation is a ratio of a number of molecules dissociated into ions to the number of all molecules of electrolyte being introduced into a solution:  $\alpha = n_{\text{dis}} / N_{\text{tot}}$  in the shares of a unit (or x 100 - in %).

The quantitative measure of electrolytic dissociation is characterized by the constant of dissociation. For example,  $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$

$$K_{\text{dis}} = K_{\text{equil}} = \frac{[\text{H}^+] \cdot [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}.$$

$K_{\text{equil}}$  shows the dissociation of a weak electrolyte, and it is called the constant of dissociation.  $K_{\text{dis}}$  depends on the nature of electrolyte and solvent, as well as on temperature, but does not depend on the concentration of electrolyte.

The more  $K_{\text{dis}}$ , is the stronger the electrolyte is, and the easier it dissociates to ions. The values of  $K_{\text{dis}}$  of weak electrolytes are given in special tables.

There is the following relation between  $K_{\text{dis}}$  and degree of dissociation  $\alpha$

$$K_{\text{dis}} = \frac{C \cdot \alpha^2}{1 - \alpha} \approx C \cdot \alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_{\text{dis}}}{C}}.$$

For very weak electrolytes  $\alpha \ll 1$ , therefore we often use

$$K_{\text{dis}} = C \cdot \alpha^2.$$

Ostwald's law of dilution: the degree of dissociation of a weak electrolyte increases with the dilution of a solution.

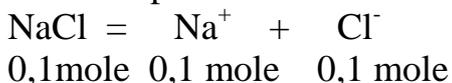
*Ionic strength.*

To assess the state of ions in solutions of strong electrolytes we use a measure called activity. Activity is an active concentration of ion, which formally replaces a concentration:  $a = f \cdot C$ , where  $f$  is a coefficient of activity, depending on ionic strength of solution  $\mu$ .

The coefficient of activity also depends on the nature of a solvent and a solute, as well as on the concentration of solution, and temperature.

An ionic strength is a characteristic of solution that takes into account concentrations of all ions in solution:  $\mu = \frac{1}{2} \sum C_i \cdot Z_i^2$ .

For example: Calculate the ionic strength of solution NaCl with  $C=0,1$  mole/l.



$$\mu = \frac{1}{2} \sum 0,1 \cdot 1^2 + 0,1 \cdot (-0,1)^2 = \frac{1}{2} \cdot 0,2 = 0,1.$$

*pH-scale of the medium.*

It is determined that,  $10^{-7}$  moles of water dissociate into ions at  $25^{\circ}\text{C}$  in 1 liter of water.

Dissociation of a weak electrolyte flows according to the equation:



One molecule of  $\text{H}_2\text{O}$  turns out on two ions of  $\text{H}^+$  and  $\text{OH}^-$ , therefore the concentration of ions in clean water equals  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$  mole/l. Because

$$K_{\text{dis}(\text{H}_2\text{O})} = \frac{[\text{H}^+] \cdot [\text{OH}^-]}{[\text{H}_2\text{O}]},$$

$$K_{\text{dis}} \cdot [\text{H}_2\text{O}] = [\text{H}^+] \cdot [\text{OH}^-] = 10^{-7} \cdot 10^{-7} = 10^{-14}.$$

$K_{\text{dis}} \cdot [\text{H}_2\text{O}] = K_w$  – ionic product of water, it is a constant value being a product of concentrations of hydrogen ions and hydro-oxide-ions in pure water or any aqueous solution at  $25^{\circ}\text{C}$ .

$$K_w = [\text{H}^+] \cdot [\text{OH}^-] = 10^{-14}.$$

If the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions are equal:

a)  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$  mole/l – the solution is neutral;

b)  $[\text{H}^+] > [\text{OH}^-]$  – the solution is acidic;

c)  $[\text{H}^+] < [\text{OH}^-]$  – the solution is alkaline.

In order to characterize the medium it is easier to use the value of pH-scale of medium. pH is the denary logarithm of concentration of hydrogen ions taken with a reverse sign:  $\text{pH} = -\lg [\text{H}^+]$  or  $\text{pOH} = -\lg [\text{OH}^-]$ ,

$$\text{pH} + \text{pOH} = 14.$$

For example: Calculate pH and pOH of NaOH solution with  $C = 0,001$  mole/l.



$$0,001 \text{ mole/l} \quad 0,001 \quad 0,001$$

a) define the ionic strength of solution :  $\mu = 1/2 \cdot (0,001 \cdot 1^2 + 0,001 \cdot (-1)^2) = 0,001$ ;

b) calculate the value of  $f_a$  for  $\mu = 0,001$  for ions with similar charges from the table:  $f_a = 0,98$ ;

c) calculate the activity value:  $a = f_a \cdot C = 0,98 \cdot 0,001 = 0,00098$ ;

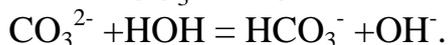
d) as  $\text{OH}^-$  is a defining ion in solutions of bases, first we find the value of  $\text{pOH} = -\lg a_{\text{OH}^-} = -\lg 0,00098 = -\lg 9,8 \cdot 10^{-4} = 3,0088$ ;

e) calculate the value of pH-scale =  $14 - 3,0088 \approx 10,99$ .

The *hydrolysis of salts* is a reaction of an exchange cooperation of salt and water which results in producing weak acid or weak base, acidic or alkaline salt.

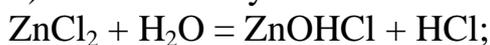
The hydrolysis is exposed to:

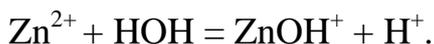
a) salt formed by weak acid and strong base:



The hydrolysis flows on an anion, the surplus of  $\text{OH}^-$  ions appears, and pH of the solution will be more than seven;

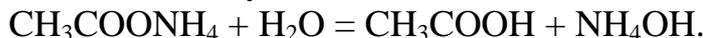
b) salt formed by weak base and strong acid:





The hydrolysis flows on cation, the surplus of  $\text{H}^+$  ions appears, and pH of the solution appears will be less seven;

c) salt formed by weak base and weak acid:



Weak acid and weak base appear in this case, and hydrolysis flows both on an anion and on cation,  $\text{pH} \approx 7$ ;

d) salt formed by strong acid and strong base, the hydrolysis does not flow, because in this case a weak electrolyte does not appear:  $\text{NaCl} + \text{H}_2\text{O} = \text{NaOH} + \text{HCl}$ ,  $[\text{H}^+] = [\text{OH}^-]$ ,  $\text{pH}=7$ .

The index of depth of hydrolysis process is *the degree of hydrolysis*: the ratio of concentration of hydrolyzed molecules to the initial concentration of solified molecules of electrolyte:

$$h = C_{\text{hyd}} / C_{\text{tot}}.$$

The constant of hydrolysis is the value determined by the nature of hydrolyzed solution of ion (cation or anion). For salts formed from weak base and strong acid, and also salts formed from strong base and weak acid the constant of hydrolysis is calculated by the following equation.

$$K_r = K_w / K_{\text{dis.ed.com.}}$$

For salts formed by weak acid and weak base

$$K_r = K_w / K_{ac} \cdot K_{bas}.$$

#### *Methods of defining the concentration of solutions.*

The concentration of a substance is the ratio of amount (mole) or mass (gramm) of the substance contained in solution to the volume or mass of solution (or solvent).

There are following methods of defining the concentration of solutions:

a) molar concentration is the number of moles of a solute, contained in 1 liter of solution

$$C_M = n(X) / V_{\text{solution}} = m(x) / M(x) \cdot V, \text{ mole/l};$$

b) molar concentration of substance equivalent (normal concentration) is the number of moles of substance equivalent, contained in 1 liter of solution

$$C_E = n_E / V_{\text{solution}} = m(X) / V \cdot M_E(X), \text{ mole/l},$$

$$M_E(x) = f_{\text{eq}} \cdot M(x), f_{\text{eq}} = 1 / z, \text{ where } z \text{ is basicity of substances};$$

c) molality of b (X) is a ratio of amount of the solute to the mass of a solvent  
m

$$b(X) = n(X) / m_{\text{solvent}} = m(X) / M(X) \cdot m_{\text{solvent}}, \text{ mole/kg};$$

d) mass portion is a ratio of mass of a given component in the solution to the total mass of a solution

$$\omega = \frac{m_{\text{solute}}}{m_{\text{solution}}}, \text{ (in the shares of a unit, } \times 100\% \text{ - in \%)}.$$

## Lecture 7. Electrochemical Processes

Lecture content: mechanism of appearance of electrode potential; Nernst's equation to calculate the measure of metallic, gaseous, and red-ox electrodes; electrolysis and Faraday's laws.

Lecture objectives: to study the laws of mutual conversion of chemical energy in to electric ones.

*Electrochemistry* is a branch of chemistry that studies the process of mutual conversion of chemical energy in to electric one. The process itself is called electrochemical.

Electrochemical processes are divided into two groups:

a) processes of conversion of chemical energy in to electrical one (galvanic elements);

б) processes of conversion of electrical energy in to chemical one (electrolysis).

There is a difference of potentials between metallic plate immersed in the solution of its own salt and solution with the formation of doubled electrical layer (DEL) that is called an *electrode potential* ( $\varphi$ ). We can write it like this:



As the ions muve in to solution  $Me^{n+}$  «->» charge of the metallic plate and «+» charge of the solution increase.

At the same time the reverse reaction flows: the reduction of  $Me^{n+}$  ions to atoms ( $Me^0$ ). At the particular moment the speed of direct and reverse processes are equalized, and an equilibrium is reestablished. The potential that is set in the equilibrium of electrode reaction is called *equilibrium electrode potential*  $\varphi$ .

The value of electrode potential  $\varphi$  depends on electrode material, nature of its medium (solution), temperature and ion concentration that the electrode exchanges with solution.

This dependence can be expressed mathematically by Nernst's equation (1888)

$$\varphi = \varphi^0 + \frac{RT}{nF} \ln a_{Me^{n+}},$$

where  $\varphi^0$  – standard potential of a given electrode measured under  $a_{Me^{n+}} = 1$  mole/l,  $T=298K$ ,  $P=101,315$  kPa;  $R$  is the universal gaseous constant that equals  $8,314$  J/(mole K);  $n$  is  $Me^{n+}$  ion charge;  $F$  is Faraday's number, equals  $96500$  Cl/mole;  $a$  is  $Me^{n+}$  activity ( or concentration), then

$$\varphi_{Me/Me^{n+}} = \varphi_{Me/Me^{n+}}^0 + \frac{R \cdot T}{n \cdot F} \ln C_{Me^{n+}}.$$

If we use these numbers, and go from natural to decimal logarithm, we get the following equation:

$$\varphi_{Me/Me^{n+}} = \varphi_{Me/Me^{n+}}^0 + \frac{0.059}{n} \lg C_{Me^{n+}}.$$

The values of standard potentials (table date) allow to define the measure of reduction and oxidation ability of metal ions: the more negative measure  $\varphi^0$  a metal has, the stronger it is, and vice versa.

It is impossible to measure the potential of separate electrode. That's why the electrode potentials are measured by comparing them with potential of electron taken for comparison, the potential of which is known.

Usually we use a standard hydrogen electrode, the value of potential of which is «0».

This electrode is referred to gaseous electrode and consists of Pt – plate that is immersed lowered into  $H_2SO_4$  solution with  $C=1$  mole/l, and it washed with the flow of gaseous  $H_2$  under pressure 101,325 kPa. The Pt-plate plays the role of a conductor of the first kind and adsorbs  $H_2$  that moves in the solution as ions, and there are «-» charged ions on Pt-plate.

Along with this the process of  $H^+$  reduction to  $H_2$  molecules flows in the opposite direction:



The scheme of electrode is  $H_2, Pt/H^+$ .

As gaseous components take place in equilibrium electrode reactions of gaseous electrodes, electrode potentials of these electrodes depend on partial pressures of gases. The equation to calculate  $\varphi$  can be expressed as following (at 298 K):

$$\varphi_{2H^+/H_2} = \frac{0,059}{2} \lg \frac{a_{H^+}^2}{P_{H_2}}. \quad \text{As } \lg a_{H^+} = -pH,$$

$$\varphi_{2H^+/H_2} = -0,0295 \lg P_{H_2} - 0,059 pH.$$

In the oxygen electrode the metallic plate (Pt, Os) goes to the contact with  $O_2$  and with the solution that contains  $OH^-$  ions. The scheme of electrode is  $O_2, Pt/OH^-$ .

At there is a reaction the oxygen electrode



To express the potential (at 298K)

$$\varphi_{OH^-/O_2} = \varphi_{OH^-/O_2}^0 + \frac{0,059}{4} \lg \frac{P_{O_2} \cdot a_{H_2O}^2}{a_{OH^-}^4},$$

as the activity of  $H_2O$  changes just a little, it is considered as a constant value, and its value is introduced to the standard potential. Then

$$\varphi_{OH^-/O_2} = \varphi_{OH^-/O_2}^0 + 0,0147 \lg P_{O_2} - 0,059 pH.$$

Along with gaseous electrodes we can use calomel and silver chloride electrodes to compare electrodes.

Oxidation-reduction electrodes are electrodes in reactions of which there is no metals and gases. As electrode we usually use Pt or Au plate that plays the role of electron conductor. But it does not take part in the reaction. The solution contains both oxidized and reduced forms of substance at the same time.

In the general form, the equilibrium on the electrode for simple systems is written as



The scheme of electrode is Pt/Ox, Red . Nernst's equation:

$$\varphi_{\text{Ox/Red}} = \varphi_{\text{Ox/Red}}^0 + \frac{2,3RT}{nF} \lg \frac{a_{\text{Ox}}}{a_{\text{Red}}}.$$

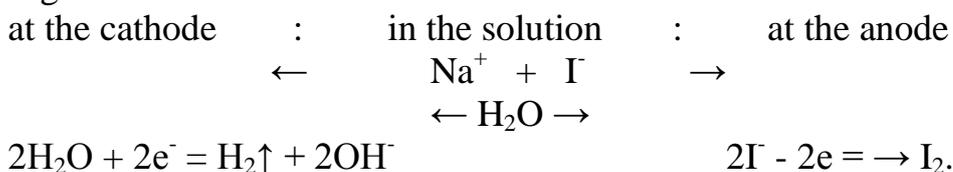
*The electrolysis* is an oxidation-reduction process that occurs on the electrodes when direct current through an ionic substance that is either molten or dissolved in a suitable solvent. There is a conversion of electric energy into chemical in electrolysis. The processes of reduction and oxidation are spatially separated: they occur at different electrodes. There is a reduction of cations at the negative electrode (cathode) and - oxidation of anions at the positive electrode (anode) . The character of electrode processes flowing in electrolysis depends on many factors: the content of electrolytes, material of electrode, regime of electrolysis (i, T).

There are two kinds of electrolysis: electrolysis of melting electrolyte and electrolysis dissolving of electrolyte. The electrolysis of aqueous solutions is complicated by water molecules that participate in electrode reactions, and capable of reducing on the cathode ( $2\text{H}_2\text{O} + 2\text{e} = \text{H}_2 + 2\text{OH}^-$ ,  $\varphi = -0,41 \text{ B}$ ), and oxidizing on the anode ( $2\text{H}_2\text{O} - 4\text{e} = \text{O}_2 + 4\text{H}^+$ ,  $\varphi = 0,814 \text{ B}$ ). There is a possibility of discharge of  $\text{H}^+$  and  $\text{OH}^-$  ions the relative concentration of which can be defined by a medium.

The process which requires the least amount of energy will occur from several possible parallel electrode processes. The criteria determining the advantages of a particular electrochemical process are the values of electrode potentials that correspond to equilibrium systems.

In general, atoms, molecules or ions having the lowest potential of the electrode are oxidized easier at the anode, and ions, molecules and atoms having the highest potential are reduced easier at the cathode.

For example, in electrolysis of neutral aqueous NaI solution water molecules will reduce at the cathode. The I ions are oxidized at the anode. We can write it as following:



To predict the qualitative results of the electrolysis of aqueous solutions of electrolytes we can use the following practical rules:

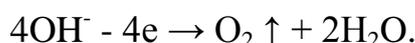
*For processes at the cathode:*

- a) cations of metals having more positive electrode potentials than hydrogen one are reduced at first (from  $\text{Cu}^{2+}$  to  $\text{Au}^{3+}$ );
- b) cations of metals having more negative electrode potentials than aluminum cannot be reduced, there is a reduction of water molecules or  $\text{H}^+$  ions at the cathode;
- c) in electrolysis of metal salts, the electrode potentials of which are between aluminum and hydrogen are released at the cathode dependently on pH medium the metal or hydrogen (gas).

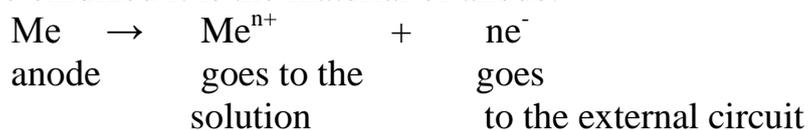
If electrolyte contains cations of different metals their reduction at the cathode flows in order of decreasing a standard electrode potential of the corresponding metal.

*For processes at the anode:* oxidation processes nature depends on the electrode material. We differ insoluble (inert) electrodes and soluble (active) electrodes. Inert electrodes are typically made of platinum, graphite, iridium. During electrolysis, they serve only to transfer electrons to an external circuit. When inert electrons are used:

- a) anions of hydrogen acids in order of increasing their potentials are oxidized firstly ( $\text{S}^{2-}$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ );
- b) during electrolysis of aqueous solutions that contain anions of oxyacids ( $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), water molecules are oxidized at the anode;
- c) hydroxide-ions are oxidized in alkaline



When soluble anodes are used made of copper, zink, nickel, silver etc. That will be oxidized it is the material of anode:



Ions of  $\text{Me}^{n+}$ , moved to the solution can be reduced at the cathode to a pure metal in the following reaction  $\text{Me}^{n+} + ne \rightarrow \text{Me}^0$ .

*The laws of electrolysis.* Quantitative characteristics of electrolysis is expressed by Faraday's two laws: a) the mass of a substance released at the electrodes is directly proportional to the amount of electricity passed through the electrolyte

$$m = E \cdot Q = E \cdot I \cdot t,$$

where  $m$  is the mass of a released substance;  $Q$  is the amount of electricity (Cl);  $I$  – the power of electricity (A);  $t$  – time (s);  $E$  – electrochemical equivalent of a substance released at the electrodes when electricity of 1 A flows in 1 sec (or the amount of electricity of 1 Cl);

b) in electrolysis of different electrolytes equal amounts of electricity release the mass of the substance at the electrodes that are proportional to molar masses of their equivalents.

It is necessary to pass the quantity of electricity equal to Faraday's number (CI 96500) through the electrolyte to transform of molar mass of equivalent of any substance.

Due to parallel secondary processes, the mass of a substance produced in electrolysis is often less than the mass which corresponds to the amount of flowing electricity. The ratio of mass of actual substance released at the electrode to the theoretical one and multiplied by 100% is called current output.

## **Lecture 8. Metal corrosion**

Lecture content: types of corrosion, kinetics of chemical and electrochemical corrosion, methods of corrosion protection.

Lecture objectives: to study the mechanism of corrosion and apply different methods of corrosion protection.

Corrosion is a process of spontaneous fracture of metals under the influence of the external environment.

The damage caused by corrosion is very great. According to reports, about one third of produced metals is eliminated from technical use due to corrosion.

The transition the metal from metallic into ionic state takes place in the process of metal corrosion. Corrosion is a spontaneous process accompanied by the decrease of Gibb's free energy ( $\Delta G^0 < 0$ ), increase of entropy of the system and by specific energy effect.

In some cases corrosion affects the entire surface of metals, in others - a part of it. The character of fracture depends on the properties of a metal and process conditions. We distinguish equal and local corrosion by the nature of metal destruction. Equal corrosion is spread over the entire surface of a metal, and local corrosion is concentrated in some areas and has different types: spots, dots, pitting, intergranular, cracking. The most dangerous types are pitting and intergranular fractures.

Chemical corrosion is corrosion caused by the interaction of a metal with dry gases or liquids, not conducting electric current. Some parts and units of machines operating in the atmosphere of oxygen, halogens at high temperatures (turbines, rocket engines, equipment at chemical plants) are subjected by chemical corrosion.

The reaction mechanism is relatively simple. The reaction products are formed on those parts of the metal surface, which react. Thus, a visible film of oxides on iron at 250-300°C metal surface is covered with the scale layer consisting of iron oxides of different degree of oxidation ( $\text{FeO}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ) at 600°C or higher. The dross can not protect a metal from further oxidation because it contains cracks or pores that allow oxygen to penetrate to the metal. When the temperature rises over 800 ° C iron oxidation rate sharply increases.

Oxide films formed on the metal often prevent further oxidation (so-called "protective" films, which prevent from penetrating both gases and liquids) to the

metal. The film that can completely cover all the metal has protective properties. Calculations show that it can be possible, if the amount of metal oxide is greater than the volume of the metal:  $V_{\text{oks}} / V_{\text{me}} > 1$ .

This condition is not met ( $V_{\text{oks}} / V_{\text{me}} < 1$ ) for the alkali and alkaline earth metals. Such films do not have the protective properties because of their chemical activity and these metals corrosion unstable.

Good protective films are formed on aluminum and chrome, so the metals are corrosive stable in atmospheric conditions (although being chemically active). Such films consist of only a few layers of molecules, and can be only detected by special optical methods.

If a metal coated by a film continues to corrode, it means that there is a diffusion of oxygen atoms through the film to the metal and the metal atoms - in the opposite direction. Diffusion of the metal and oxygen can occur in the protective layer of the solid oxide by one of two possible ways:

- a) movement of ions in the interstitial space of the crystal lattice;
- b) movement of ions through empty lattice sites.

The first mechanism occurs during films formation of ZnO, CdO, BeO, Al<sub>2</sub>O<sub>3</sub>; the second - Cu<sub>2</sub>O, FeO, NiO, CoO, ZrO<sub>2</sub>, TiO<sub>2</sub>.

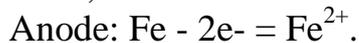
The diffusion of cations in the protective film is accompanied by a simultaneous movement in the same direction of the equivalent number of electrons in the interstices in the first way and by "electronic defects" (cation of higher valence) in the second way. With increasing temperature the air oxidation of metals is more intensive (the diffusion rate is increased).

Destruction of metal in contact with the electrolyte, followed by the appearance of an electric current is called electrochemical corrosion.

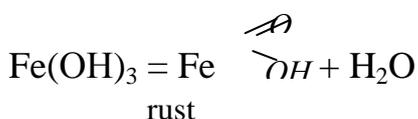
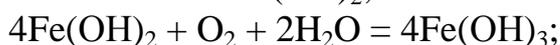
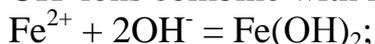
In the atmospheric conditions a water film plays the role of an electrolyte on a metal surface. The electrodes are typically a metal itself and impurities contained in it.

The mechanism of corrosion in acidic and neutral media is different.

Let's consider technical iron corrosion in the air when it is covered with a wet film or in solution with a low concentration of hydroxid- ions. As used herein the anode base metal is iron, the cathode is impurities contained in the metal, e.g., graphite grains. But graphite grains will not participate in the reduction reaction at the cathode, and the reaction will proceed with electrolyte, in this case water.



OH<sup>-</sup> ions combine with Fe<sup>2+</sup> ions moving into the solution



According to the theory of electrochemical corrosion of a metal in contact with an electrolyte many galvanic elements appear on the surface of metal. In this case, the metal is the anode and the cathode is impurities and metal segments having more positive potential. Machining of the metal changes its electrode potential, so the contact of two metal portions, deformed and undeformed, is enough for the appearance of the potential difference. A deformed portion will corrode with the film. The potential difference arises at touching portions naked and covered.

Since ions and molecules that bind electrons in the cathode process are called depolarizers, we often speak of hydrogen depolarization in acidic and neutral oxygen depolarization and weakly alkaline media.

Since electrochemical corrosion is caused by galvanic cells activity, we can conclude that the factors contributing the activity of galvanic elements enhance corrosion. The corrosion rate is the greater the farther the metals are in the electrochemical series from which galvanic couple is formed. The corrosion rate increases with increasing temperature and increasing concentration of the oxidant in the solution.

Often the corrosion products are poorly soluble in a given medium environment and their presence protects a metal from further destruction. For example, such metals as iron in an alkaline medium and lead in dilute sulfuric acid will not corrode, due the protective film formed of iron hydroxide and lead sulfate on their surfaces.

Electrode polarization, the formation of films on metal surface, hydrogen overvoltage are of great importance in the corrosion process. If polarization of electrodes didn't happens, the corrosion process would proceed at such a rate that iron and other metals would lose their meaning in technology.

Underground corrosion. The destruction of oil and gas pipelines, cable sheaths, metal constructions, piles (soil corrosion) occurs under the influence of substances soluble in the soil or under the influence of stray currents. The intensity of soil corrosion depends on the aggressive action of acids, organic compounds and from the activity of bacteria. Peaty and marshy soils are considered the most active ones.

Stray currents coming from electrical installations operated by direct current trams, metro, electric railway, cause the appearance of DC input and output spots, on metal objects (pipes, cables, rails), that is, the formation of cathodic and anodic zones on the metal (anode zone - output current place). Stray currents from the AC power sources cause a slight corrosion of steel products and a strong one- in products from ferrous metals.

Chlorine, ions, bromine and iodine increased dramatically the corrosion.

The following methods are widely used to protect metal constructions from corrosion: protective coatings; anticorrosive alloying metal; electrochemical protection; processing the corrosive environment; development and production of new metal construction materials with increased corrosion resistance.

Selection of one of the protective methods is not only based on technical considerations, but also on economic calculations. The cheapest and most common method paint-and lacquer is coatings.

Such metals as aluminum, iron, copper and magnesium are covered with artificially passive films. Heat-resistant alloying widely used, that is alloying components to increase heat resistance are introduced into alloys. For example, to improve corrosion resistance of steel some alloying elements - chromium, nickel, titanium, tungsten are introduced in it the presence of which provides the appearance of continuous passive films on the surface.

Metal coating is used to prevent corrosion. By the nature of the protective effect we distinguish anode and cathode coating. Anode coating on the protective metal is made of a metal with more negative electrode potential (iron covered with zinc). Cathode coating on the protective metal is made of a metal with more positive electrode potential (iron covered with nickel).

To protect a metal against corrosion inhibitors are also introduced into a corrosion medium.

Inhibitors are divided into vapor phase inhibitors (or volatile) and liquid phase ones. Anionic inorganic inhibitors (nitrites, chromates, phosphate) are mainly used as liquid phase inhibitors for neutral solutions.

Their inhibitory effect promotes the formation of oxide films, or films of sparingly soluble compounds, whereby the potential is shifted to more positive values. Acid corrosion inhibitors, are generally organic compounds which absorbing on metal surface inhibit both anodic and cathodic process.

An electrochemical method is used in aggressive environments (sea water, soil) of protection. A so-called sacrificial protection is often used in industry. Aluminum plate of zinc or zinc are attached to the steel hull construction of a ship plates of zinc or zinc. A microgalvanic element is formed where zinc plays the role of anode and the shielded construction becomes a cathode. So, the corrosion is reduced and stopped because of shift of the potential.

A similar result can be achieved in other methods, called cathodic protection by the addition of a metal to be protected to the negative pole of an external source.

Metals such as titanium, nickel, stainless steel, may be protected from corrosion by attaching them to the positive pole of the generator (so-called anodic protection). Anodic current density is brought up to the value which leads to a complete passivation, as a result the metal ceases to dissolve. This method is used to protect constructions from corrosion in very harsh environments.

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Karlygash Sadyrovna Idrissova  
Aytbala Aytenovna Tumanova

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