

CONCISE THEORETICAL MATERIAL

1 s-Elements. Biological role, application in medicine.

Elements of IA-group Li, Na, K, Rb, Cs, Fr, elements of IIA-group, Be, Mg, Ca, Sr, Ba, Ra as well as hydrogen and helium belong to the block of s-elements. The electronic formula of the external shell of IA-group elements and hydrogen is ns^1 and of the elements of IIA group and helium - ns^2 , where “n” is the number of the period.

Chemical properties of s-elements of IA and IIA-groups are similar. s-Block elements easily give their valences-electrons, which means that they are strong reducers. Stable ions with an external electronic shell of the previous inert gas are formed by losing their s-electrons.

Radiuses of the ions increase in groups by growth of the atomic number of an element and decrease at transition from IA to IIA-group. The closeness of ionic radiuses of Li^+ , K^+ , Ba^{2+} plays an important role in the biochemistry of these metals.

S-Block elements are characterized by small ionization energy at big radiuses of atoms and ions. Mainly s-elements form compounds with ionic bonds, except of hydrogen, whose connections even with the elements with the greatest electronegativity is characterized by a covalent bond.

Hydrogen is the first element of the periodic table of elements. Fraction of total mass of Hydrogen in the Earth's crust is 1%-this is the 10th most prevalent element. However, its role in nature is not determined by the weight, but by the number of atoms, which amount among other elements is 17% (second place after oxygen-52%). So the importance of hydrogen in chemical processes occurring on the Earth is as great as the importance of Oxygen. Almost all hydrogen on Earth exists in the form of compounds and only very small number of hydrogen is contained in atmosphere in form of a simple substance (0.00005% in volume).

Hydrogen is a part of almost all organic substances and is present in all living cells. In living cells the number of atoms of hydrogen is nearly 50%.

Hydrogen is used in such industries as: chemical industry (production of ammonia, methanol, soap and plastic), food industry (registered as a food additive E949), and aviation industry.

Electron configuration of atoms of hydrogen is $1s^1$. Hydrogen similar to alkaline metals is univalent and has reducing properties. Hydrogen has three isotopes: protium 1_1H , deuterium 2_1H and tritium 3_1H .

Hydrogen concentration in the human body is approximately 10%, that comparing to its content in the Earth's crust (1%) demonstrates its exceptional role in the human body. In human organism hydrogen exists in the form of different compounds, for example water.

Sodium, potassium.

Na^+ and K^+ ions are always together in the geosphere and their separation is a difficult process, on the contrary in the biosphere these ions are distributed on different sides of the cell membrane as they relate to the extracellular (sodium) and intracellular (potassium) cations.

These ions continuously move on ion channels in both directions, down a concentration gradient. This is the movement from a region of high substance density (prevalence) to a region of low density (prevalence). Such process can't proceed spontaneously, that is why the energy for it is reported by reaction of ATP hydrolysis. K^+ penetrates into cells thanks to affinity to the protein membrane - phosphoprotein. ATP hydrolysis takes place in a cell with the formation of ADP (adenosine diphosphate acid), the released PO_4^{3-} -group phosphorylate phosphoprotein, and it "releases" K^+ ion into intracellular space. As a result phosphorylated phosphoprotein has an increased affinity for Na^+ ion, it captures the ion and "goes" with it outside, where "releases" the ion into the extracellular space. This is one of the simplified work schemes of sodium-potassium pump, whose main task is to maintain the balance of potassium and sodium in all systems of the body. Firstly, this balance provides the maintenance of required osmotic pressure in bioliquids, which is the driving force of all absorption and excretion processes; Secondly, this balance keeps pH

values of each organ and tissue. Thirdly, sodium and potassium play a very important role in the transmission of nerve impulses.

By "ionophore" mechanism the K^+ ions fall into the central cavity of the lipid membrane, which is about 1 nm in diameter and contains hydrated K^+ ion. Polypeptide spiral, which forms this cavity, has an electrostatic charge which is able to keep such number of K^+ ions, that corresponds to approximately 2 mol/l concentration. Then the central cavity is compressed and turns into a narrow channel-filter, which omits only already dehydrated K^+ ions. This filter has 4 places to link K^+ thanks to peptide groups $C=O$, and the coordination number of K^+ is equal to 8. In the same conditions the Na^+ ions are not associated, that provides the selectivity of cavity to K^+ in 104 times.

It should be noted that the ions of Rb^+ and Cs^+ can be linked by carbonyl groups in a membrane cavity that allows to use them as probes in the study of cell membrane channels. When linking K^+ the internal charge of the cavity changes and it lets in and lets out K^+ ions from a cell.

It is possible to explain the action of sodium-potassium pump differently, considering ability of cellular membranes "to be turned inside out" at a change of an electrostatic charge on its surface.

Magnesium, calcium

Inside the cell the amount of Mg^{2+} is many times more, than in the extracellular space, when Ca^{2+} is predominantly extracellular cation. Mg^{2+} ion is a stronger complex former than Ca^{2+} ion. It serves as the center of some metal-enzymes, for example, catalyzes an important hydrolysis of ATP. Magnesium complex with ATP is a part of substrate kinase enzyme responsible for the transfer of phosphate groups. Kinases are controlled by calmodulin and other proteins and are the basis of the signal system in higher organisms.

In the plant world Mg^{2+} is the part of coordination centre of two main enzymes that control such global process as photosynthesis, which is to make H_2O and CO_2 into carbohydrates and O_2 by the influence of light energy. In photosynthesis, which can occur in the dark (so-called "dark phase"),

magnesium is the center of the enzyme containing ribulose-1,5-diphosphate-carboxylate, which is called rubisco. This enzyme is very common in biosphere and controls the binding of atmospheric CO₂ (~ 1011 tons per year!). In the original form of enzyme the Mg²⁺ ion (with coordination number equal to 6) coordinates carboxyl groups of glutamic and aspartic acids, 3 molecules of water and the residue of lysine carbamate.

By the way carbamate is formed by the reaction of the original CO₂ portion with the terminal amino group of lysine, so already present CO₂ "runs" the mechanism of photosynthesis.

The content of Ca²⁺ in the body is ~1%, calcium- is the fifth element on prevalence after C, H, O, N. In mammals organism 95% of calcium is placed in solid tissues: bones and teeth, where it exists in the form of fluorapatite Ca₅(PO₄)₃F and hydroxyapatite Ca₅(PO₄)₃OH; in birds and shellfish organisms it exists in the form of CaCO₃. In the blood vessels and arteries, calcium is present in the form of CaCO₃ or the complex with cholesterol.

Ca²⁺ ions form not very strong coordination compounds, have low values of formation constants and variable coordination number (6 and 8), have moving coordination sphere, as well as the high speed exchange of ligands. Therefore, calcium complexes are suitable for signal systems, regulate the reduction of muscle fibers, activate many enzymes, and define the process of blood clotting.

The concentration of Ca²⁺ in the body is regulated by parathyroid hormone - calcitocin and its absorption is determined by the content of vitamin D in the body. The lack of this vitamin decreases the absorption of Ca and manifests itself in the form of the rickets disease. Ca is an extracellular element; its concentration in the cell is small: ~ 10⁻⁷ mol/l, and outside the cell ~ 10⁻³ mol/l, a concentration gradient is maintained thanks to Ca-pump.

The most studied Ca-containing enzyme is calmodulin. It activates a protein kinase, catalyzes the protein phosphorylation, activates Fe-containing enzyme NO-synthase. In calmodulin Ca²⁺ ion has a coordination number equal

to 6 and is surrounded by three monodentate carboxyls of asparagin acid, a bidentate fragment of glutamin acid and a water molecule.

2. P-block elements. Biological role, application in medicine.

30 elements of IIIA-VIIIA group of the periodic system belong to p-elements; the p-elements enter into (II) and (III) short periods, as well as in the V-VI big periods. Elements of III-A group have one electron on the p-orbital. In other groups IVA-VIIIA there is a consecutive filling of the p-sublevel to 6 electrons.

Among p-elements there are elements that can be both cations and anions (Al, Ca, Ti, Se, Pb, Bi, Sb, Bi) or only anions (B, C, Si, N, P, As, O, Te, P, Cl, Br, I, At). All cations, except $Al^{3+}(1s^22s^22p^6)$ have a structure of external electronic shell $(n-1)d^{10}ns^2$, where n is the number of period. Increased stability characterizes external electronic shell of elements of VI period because $6s^2$ electrons are preceded by $4f^{14}5d^{10}$ electrons, which shield the nucleus.

In the period from left to right atomic radii of p-elements decrease with the increase of nuclear charge and increase with the increase of ionization energy (E_I) and electron affinity (E_a); electronegativity (EN) increases and oxidative activity of simple substances and non-metallic properties become stronger. In groups with the increase of sequence number the radius of atoms and ions also increases. Ionization energy in transition from 2p-elements to 6p-elements decreases. With an increase of number of p-element in the group the non-metallic properties become weaker, and metal properties become stronger. The properties of p-elements and their compounds are influenced both by the appearance of new sublevels in the external electronic shell and by the filling of sublevels of internal electronic shells. Properties of p-elements of the second period B, C, N, O, F differ from the properties of elements of other periods. So, starting with the p-elements of the third period, we receive free p-sublevel, on which electrons from 5s-sublevels can move to (when atoms are excited). Fully