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Medical Chemistry: Theory and Laboratory Exercises for the First Module

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Навчально-методичний посібник складається з теоретичного матеріалу та лабораторних робіт, і відповідає програмі першого модуля курсу "Медична хімія" для студентів медичного профілю вищих навчальних закладів України. У ньому міститься матеріал, що відноситься до таких розділів: хімічні елементи та періодична система елементів, хімічний зв'язок та комлексоутворення, електролітична дисоціація у розчинах, кислотність та кислотно-основні рівноваги у розчинах, колігативні властивості розчинів.

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Manual includes theory and laboratory exercises for the first module of course "Medical Chemistry" for students of medical specialities of universities. It consists of material on selected topics: chemical elements and periodic table of the elements, chemical bonding and complex formation, electrolytic dissociation, acidity and acid-base equilibria in solutions, colligative properties of solutions.

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THEME 1. CHEMICAL ELEMENTS. PERIODIC TABLE

Atoms, molecules and ions

All atoms can be distinguished by the number of protons and neutrons they contain. The *atomic number* (Z) is the number of protons in the nucleus of each atom of an element. As atom is a neutral particle the number of protons is equal to the number of electrons, so the atomic number also shows the number of electrons in the atom.

The chemical identity of an atom can be determined solely from its atomic number. For example, the atomic number of oxygen is 8. This means that each oxygen atom has 8 protons and 8 electrons so each atom in the universe that contains 8 protons is oxygen.

The mass number (A) of an atom is the total number of neutrons and protons present in the nucleus of an atom of an element. The number of neutrons in an atom is equal to the difference between the mass number and the atomic number. If we have oxygen atom for which mass number is 16, this means the atom has 8 neutrons.

A *molecule* is an aggregate of at least two atoms in a definite arrangement held together by chemical forces (also called chemical bonds). A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio.

An *ion* is an atom or a group of atoms that has a net positive or negative charge. The number of positively charged protons in the nucleus of an atom remains the same during ordinary chemical changes (called chemical reactions), but negatively charged electrons may be lost or gained. The loss of one or more electrons from a neutral atom results in a *cation*, an ion with a net positive charge. The acceptance of electron(s) by an atom results in an *anion*, a particle with a net negative charge.

Periodic law and periodic table

Recognition of periodic regularities in physical and chemical behavior and the need to organize the large volume of available information about the structure and properties of elemental substances led to the development of the periodic law by Russian chemist D. I. Mendeleev. The modern formulation of *periodic law* states that the physical and chemical properties of

elements are periodic functions of their atomic numbers. It is important to remember that the periodic table of elements was organized by Mendeleev according to increasing atomic weights, and not by atomic number.

Visual expression of the periodic law is the periodic table – a chart in which elements having similar chemical and physical properties are grouped together. The periodic table is a handy tool that correlates the properties of the elements in a systematic way and helps us to make predictions about chemical behavior.

The modern periodic table is presented in Appendix on the page 45. In the table the elements are arranged by atomic number (shown above the element symbol) in horizontal rows called *periods* and in vertical columns known as *groups* or *families*, according to similarities in their chemical properties. All elements can be divided into three categories – *metals*, *nonmetals*, and *metalloids*. Elements are often referred to collectively by their periodic table group number (Group 1, Group 2, and so on). However, for convenience, some element groups have been given special names. The Group 1 of the elements (Li, Na, K, Rb, Cs, and Fr) are called *alkali metals*, and the Group 2 elements (Be, Mg, Ca, Sr, Ba, and Ra) are called *alkaline earth metals*. Elements in Group 17 (F, Cl, Br, I, and At) are known as *halogens*, and elements in Group 18 (He, Ne, Ar, Kr, Xe, and Rn) are called *noble gases* (or *rare gases*).

Valence electrons and chemical properties of the elements

The chemical reactivity of the elements is largely determined by their *valence electrons*, which are the outermost electrons. For the representative elements, the valence electrons are those in the highest occupied shell. All nonvalence electrons in an atom are referred to as core electrons. Looking at the electron configurations of the representative elements, a clear pattern emerges: all the elements in a given group of the periodic table have the same number and type of valence electrons. The similarity of the valence electron configurations is what makes the elements in the same group resemble one another in chemical behavior. Thus, for instance, the alkali metals (the Group 1 in the periodic table) all have the valence electron configuration of ns^1 and they all tend to lose one electron to form the unipositive cations. Similarly, the alkaline earth metals (the Group 2 of the elements) all have the valence electron configuration of ns^2 , and they all tend to lose two electrons to form the dipositive cations. As a group, the noble

gases behave very similarly. Helium and neon are chemically inert, and there are few examples of compounds formed by the other noble gases. This lack of chemical reactivity is due to the completely filled *ns* and *np* subshells, a condition that often correlates with great stability. Although the valence electron configuration of the transition metals is not always the same within a group and there is no regular pattern in the change of the electron configuration from one metal to the next in the same period, all transition metals share many characteristics that set them apart from other elements. The reason is that these metals all have an incompletely filled *d* subshell. Likewise, the lanthanide (and the actinide) elements resemble one another because they have incompletely filled *f* subshells.

Review questions for the theme 1.

- 1. Give the definitions of terms: a) atomic number, b) mass number. Write the interrelation between the mass number and the atomic number of an element.
- 2. Give the definitions of terms: a) molecule, b) cation, c) anion. Write examples.
- 3. What are the valence electrons? Write in general the configurations of valence electrons for the elements: a) alkali metals, b) alkaline earth metals, c) halogens, d) noble gases.
- 4. State the periodic law. What is the periodic table of the elements? What are the groups and periods of the periodic table?
- 5. Identify the atoms using their ground-state electron configurations: a) $1s^22s^1$, b) $1s^22s^22p^2$, c) $1s^22s^22p^64s^1$.

Further readings

- 1. Chang R. Chemistry. 10-th edition. NY: McGraw-Hill, 2010. 1170 p.
- 2. Lewis R., Evans W. Chemistry. 3-rd ed. Palgrave Macmillan, 2006. 463 p.
- 3. Sarker S.D., Nahar L. Chemistry for pharmacy students: general, organic and natural product chemistry. Chichester: John Wiley & Sons, 2007. 383 p.

THEME 2.

PROPERTIES AND QUALITATIVE REACTIONS OF SOME IMPORTANT IONS

Qualitative analysis consists of methods for establishing the qualitative chemical composition of a substance – that is, the identification of atoms, ions, and molecules that present in the substance being analyzed. The most important characteristics of all methods of qualitative analysis are *specificity* and *sensitivity*. *Specificity* characterizes the ability to detect the presence of an unknown element in the presence of other elements – for example, iron in the presence of nickel, manganese, chromium, vanadium or silicon. *Sensitivity* is defined as the smallest quantity of an element that can be detected by a given method.

LABORATORY EXERCISE NO.1.

Properties and qualitative reactions of CO_3^{2-} , SO_4^{2-} , NO_2^{-} , $S_2O_3^{2-}$ ions

Objective: Investigation of qualitative reactions of carbonate, sulphate, nitrite and thiosulphate anions.

Theoretical background

A carbonate is a salt of carbonic acid, H₂CO₃, characterized by the presence of the carbonate ion, CO₃²⁻. The name may also mean an ester of acid. organic compound containing carbonic an the carbonate group $C(=O)(O-)_2$. Metal carbonates generally decompose on heating, liberating carbon dioxide and leaving behind an oxide of the metal. In aqueous solution, carbonate, bicarbonate, carbon dioxide, and carbonic acid exist together in dynamic equilibrium. In strongly basic conditions, the carbonate ion predominates, while in weakly basic conditions, the bicarbonate ion (HCO₃⁻) is prevalent. In more acid conditions, aqueous carbon dioxide, $CO_2(aq)$, is the main form.

A sulphate is a salt of sulphuric acid, H₂SO₄. Many examples of ionic sulphates are known, and many of these are highly soluble in water. Exceptions include calcium sulphate, strontium sulphate, lead (II) sulphate and barium sulphate, which are poorly soluble. The barium derivative is

useful in the gravimetric analysis of sulphate. In the test for the sulphate ion, when BaCl₂ is added, the formation of a white powdery precipitate indicates the presence of the sulphate ion. Barium chloride gives white precipitate also in the presence of carbonate-anion, but the barium carbonate is soluble in hydrochloric acid while the barium sulfate is not.

Nitrite anion can be oxidized or reduced, with the product somewhat dependent on the oxidizing/reducing agent and its strength. The formal oxidation state of nitrogen atom in a nitrite is +3. This means that it can be either oxidized to oxidation states +4 and +5, or reduced to oxidation states as low as -3.

The nitrite ion gives several reactions based on its redox properties.

When it reacts with the I^- anion, the nitrite ion is being reduced to nitric monoxide.

In thiosulphate the prefix thio- indicates that thiosulphate ion is a sulfate ion with one oxygen replaced by a sulphur.

Thiosulphates are stable only in neutral or alkaline solutions, but not in acidic solutions due to decomposition to sulphite and sulphur, the sulphite being dehydrated to sulphur dioxide:

$$S_2O_3^{2-} + 2H^+ \rightarrow SO_2 + S + H_2O_2$$

$$SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O.$$

Thiosulphate ion is reducing agent. For example, it can reduce iodine in solution or I_3^- ions to iodide ion, this reaction is accompanied by lose of solution color

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2 I^-.$$

It should be noted that this is not a confirmatory test for thiosulphate ion because many reducing agent can do this.

Experiments

Carbonate ion
$$CO_3^{2-}$$

Add 5-6 drops of sodium carbonate solution to a test tube. Dilute it by 2-3 ml of distilled water and add few drops of barium chloride.

Carbonic acid is unstable at room temperature, so it decomposes readily to CO₂ and water. Thus, another type of qualitative reaction on carbon-

ate-anion includes adding of a strong acid (hydrochloric acid) to a solid salt.

Remove the liquid over resulting precipitate, and add several drops of concentrated solution of hydrochloric acid.

Describe all changes and write down equations of chemical reactions.

Sulphate ion SO_4^{2-}

Add 5-6 drops of sodium sulphate solution to a test tube. Dilute this with 2-3 ml of distilled water and add few drops of barium chloride.

Remove the liquid over resulting precipitate, and add several drops of concentrated solution of hydrochloric acid.

Describe all changes and write down equations of chemical reactions.

*Nitrite ion NO*₂

- 1) To a test tube containing 2-3 ml of water solution of sodium nitrite add few drops of acetic acid, and then add few drops of potassium iodide solution.
- 2) Another qualitative reaction of nitrite ion includes forming of potassium cobaltinitrite ($K_3[Co(NO_2)_6]$). To a test tube containing solid sodium nitrite (20-30 mg) add 3 ml of distilled water and 5-6 drops of acetic acid. Then add 2-3 drops of potassium acetate solution and 2-3 drops of cobalt (II) chloride solution, shake the resulting solution well.

Describe all changes and write down equations of chemical reactions.

Thiosulphate ion $S_2O_3^{2-}$

- 1) Prepare the solution of sodium thiosulphate by dissolving of 20-30 mg of solid salt in 2-3 ml of distilled water. After that add dropwise concentrated sulphuric acid. Observe changes.
- 2) To 2-3 ml of the solution of sodium thiosulphate add 1-2 drops of iodine solution in alcohol or in water with potassium iodide. Observe changes.

Describe all changes and write down equations of chemical reactions.

Questions for the laboratory exercise No.1

1. What kind of chemical reactions are called qualitative reactions?

- 2. Aqueous solution of two salts Na₂CO₃ and Na₂SO₄ is given. How to prove the simultaneous occurrence of both carbonate and sulphate anions?
- 3. On which properties based qualitative reactions of nitrite ion?
- 4. What features should have qualitative reactions?
- 5. Describe the differences in chemical properties of sulphate and thiosulphate anions.

LABORATORY EXERCISE NO.2.

Properties and qualitative reactions of MnO₄, Fe³⁺, Cu²⁺, Ag⁺ ions

Objective: Investigation of qualitative reactions of Cu(II), Ag(I) and Fe(III) cations and MnO₄⁻ anion.

Theoretical background

Permanganate is general name for a chemical compounds containing the manganese in +7 oxidation state, for example, MnO_4^- ion. The color of solution containing permanganate ion is dark violet. Permanganate ion is a strong oxidizing agent because here the manganese is in the highest oxidation state. The exact chemical reaction of reducing of MnO_4^- is dependent upon the reducing agent utilized and the acidity of solution.

In an acidic solution, permanganate ion is usually reduced to the colorless Mn²⁺ ion:

$$8H^{+} + MnO_{4}^{-} + 5\bar{e} \rightarrow Mn^{2+} + 4H_{2}O.$$

In a strongly basic solution, permanganate ion is reduced to the manganate ion (MnO_4^{2-}) in which the manganese is in +6 oxidation state:

$$\text{MnO}_4^- + \bar{e} \rightarrow \text{MnO}_4^{2-}$$
.

The color of solution containing MnO_4^{2-} is green.

In a neutral medium, however, MnO_4^- is reduced to brown unsoluble manganese dioxide (MnO_2) in which the manganese is in +4 oxidation state:

$$2H_2O + MnO_4^- + 3\bar{e} \rightarrow MnO_2 \downarrow + 4OH^-.$$

Copper (II) ions correspond to weak insoluble base Cu(OH)₂ which can be dissolved, however, in the presence of excess of ammonia or other complexants. In the test for the presence of copper (II) ions the clear light blue solution of copper (II) sulfate will change to a milky light blue and then to a clear, deep blue when ammonia is added.

Aqueous solution of iron (III) compounds easily undergo hydrolysis and, as a result of it, the brown precipitate appears on vessel walls.

Iron (III) ion corresponds to brown unsoluble hydroxide Fe(OH)₃, which is not soluble in excess of NH₃ or NaOH.

Iron (III) cations give deep blue precipitate at addition of potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$.

Silver ion shows strong oxidizing properties due to its high redox potential. But the simplest qualitative reactions of Ag⁺ ions are based on precipitation reactions. Silver halides (except AgF) are highly insoluble in aqueous solutions and are used in gravimetric analytical methods.

Qualitative reaction of Ag⁺ ions is precipitation of silver chloride from a silver containing medium by adding of few drops of any chloride solution. In the same conditions the addition of iodide anion gives yellow precipitate of AgI. White precipitate of AgCl is soluble in excess of ammonia or sodium thiosulfate.

Experiments

Permanganate ion MnO₄⁻

Add 1-2 drops of potassium permanganate solution into three test tubes. Dilute it with 2-3 ml of water. Then add to the first test tube crystalline sodium sulphite (Na₂SO₃); to the second test tube add 2-3 drops of sodium hydroxide solution and than crystalline sodium sulphite; to the third one add 2-3 drops of sulphuric acid and than crystalline sodium sulphite.

Describe all changes and write down equations of chemical reactions.

Copper ion Cu²⁺

To the aqueous solution of copper sulphate (2-3 ml) in a test tube add 1-2 drops of aqueous ammonia. Shake it gently and try to dissolve resulting precipitate with an excess of ammonia.

Describe all changes and write down equations of chemical reactions.

*Iron ion Fe*³⁺

To test for presence of iron (III) ion add 1-2 drops of potassium thio-cyanate (KSCN) solution to the solution of iron (III) chloride (1-2 ml) to get a blood red color. Add 5-6 drops of sodium fluoride solution to the resulting solution until the mixture will turn to colorless transparent solution.

To a test tube with 1-2 ml of iron (III) chloride solution add 1-2 drops of hydrochloric acid and then add 1-2 drops of potassium hexacyanoferrate (II) solution $(K_4[Fe(CN)_6])$.

Describe all changes and write down equations of chemical reactions.

Silver ion Ag^+

Add 1 ml of silver nitrate solution into two test tubes. Then to the first test tube add sodium chloride solution (3-4 drops) and to the second one potassium iodide solution (3-4 drops).

Describe all changes and write down equations of chemical reactions.

Questions for the laboratory exercise No.2

- 1. Explain the differences in oxidizing properties of potassium permanganate on the basis of results of experiments.
- 2. Describe the colors of compounds containing manganese in different oxidation state.
- 3. Explain, why the precipitate of copper hydroxide is soluble in the presence of ammonia.
- 4. How to explain color changes in the experiments with iron (III) chloride?
- 5. Is it possible to provide qualitative reactions (which are described above) on Cu(II), Ag(I) and Fe(III) ions if they are present in one solution?

Further readings

- 1. Chang R. Chemistry. 10-th edition. NY: McGraw-Hill, 2010. 1170 p.
- 2. Atkins P., de Paola J. Physical Chemistry for the Life Sciences. W.H.Freeman Publishers, 2006. 624 p.

THEME 3. CHEMICAL BONDING

Chemical bond

Atoms of most elements can interact with one another to form compounds. The forces that hold these atoms together in compounds are called *chemical bonds*. When atoms interact to form a chemical bond, only their outer electronic shells are in contact. For this reason, when we study chemical bonding, we are concerned with the valence electrons of the atoms.

Ionic bond

An *ionic bond* is the electrostatic force that holds ions together in an ionic compound. Consider, for example, the reaction between lithium and fluorine to form lithium fluoride. The electronic configuration of lithium is $1s^22s^1$, and that of fluorine is $1s^22s^22p^5$. When lithium and fluorine atoms come in contact with each other, the outer $2s^1$ valence electron of lithium is transferred to the fluorine atom. After this process the ions with stable electronic configurations are formed. The lithium cation (Li⁺) has electronic configuration like helium atom, $1s^2$; the fluorine anion (F⁻) – like neon, $1s^22s^22p^6$. The ionic bond in LiF is formed by the electrostatic attraction between the positively charged lithium ion and the negatively charged fluoride ion. The compound itself is electrically neutral.

· Li
$$+$$
 : $\overset{\dots}{F}$ · \longrightarrow Li⁺ : $\overset{\dots}{F}$: $^-$ (or LiF)
 $1s^22s^1$ $1s^22s^22p^5$ $1s^2$ $1s^22s^22p^6$
· Ca · $+$ · $\overset{\dots}{O}$ · \longrightarrow Ca²⁺ : $\overset{\dots}{O}$: 2 · $^-$
[Ar] $4s^2$ $1s^22s^22p^4$ [Ar] [Ne]

Ionic bonding occurs between elements when the energy required to remove the outer shell electrons (the ionization energy) of one of reacting elements is relatively low. Elements with such low ionization energies are metals. Therefore, compounds containing a metal tend to be ionic. Nonmetals generally contain more than three electrons in the outer shells of their atoms and have high tendency to accept electrons from another atoms. Consequently substances formed by typical metals and nonmetals are ionic.

Covalent Bond

When two or more non-metals combine their atoms have to share electrons forming common electronic pair and achieving the stable electronic configuration of a noble gas. This type of bonding is called *covalent bonding*. So in this type of chemical bond two electrons are shared by two atoms. Covalent compounds are substances that contain only covalent bonds. For the simplicity, the shared pair of electrons is often represented in the molecule by a single line. Thus, the covalent bond in the hydrogen molecule can be written as H–H, in hydrogen chloride molecule as H–Cl.

In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms in the molecule together and is responsible for the formation of covalent bonds in other molecules. Covalent bonding between many-electron atoms involves only the valence electrons.

Consider, for example, the fluorine molecule, F_2 . The electron configuration of F atom is $1s^22s^22p^5$. The 1s electrons are low in energy and stay near the nucleus most of the time. For this reason they do not participate in bond formation. Thus, each F atom has seven valence electrons (the 2s and 2p electrons), but there is only one unpaired electron on F, so the formation of the F_2 molecule can be represented as coupling and sharing of these electrons. Note, that only two valence electrons participate in the formation of F_2 . The other, nonbonding electrons, are called *lone pairs* – pairs of valence electrons that are not involved in covalent bond formation. Thus, each F atom in F_2 molecule has three lone pairs of electrons.

$$: \overrightarrow{F} \cdot + \cdot \overrightarrow{F} : \longrightarrow : \overrightarrow{F} : \overrightarrow{F} : \text{ or } : \overrightarrow{F} - \overrightarrow{F} :$$

$$\text{lone pairs} \longrightarrow : \overrightarrow{F} - \overrightarrow{F} : \longleftarrow \text{lone pairs}$$

If two atoms are held together by one electron pair the bond is called a *single* bond. Sometimes, more than one pair of electrons is shared. Consider, for example, oxygen gas molecule, O_2 . Here, each oxygen shares two pairs of electrons to achieve the electron configuration of neon. The structural formula of this oxygen molecule is written O=O. If two atoms share two pairs of electrons, the covalent bond is called a *double* bond. Double bonds exist in molecules of carbon dioxide and ethylene. In a molecular

structure, where three pairs of electrons are shared, the bond is called a *tri*ple bond, for example in nitrogen molecule, N_2 .

The formation of these molecules illustrates the *octet rule*: an atom of s-and p-elements (other than hydrogen) tends to form bonds until it is surrounded by eight valence electrons. In other words, a covalent bond forms when there are not enough electrons for each individual atom to have a complete octet. By sharing electrons in a covalent bond, the individual atoms can complete their octets. The requirement for hydrogen is that it attain the electronic configuration of helium, or a total of two electrons.

Multiple bonds are shorter than single covalent bonds. *Bond length* is defined as the distance between the nuclei of two covalently bonded atoms in a molecule. For a given pair of atoms, such as carbon and nitrogen, triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds. The shorter multiple bonds are also more stable than single bonds.

For the predicting whether compounds are ionic or covalent we use general rule:

 $metal + non-metal \rightarrow ionic bonding,$

non-metal + non-metal \rightarrow covalent bonding.

Oxidation number (oxidation state) refers to the number of charges an atom would have, if electrons were transferred completely to the more electronegative of the bonded atoms in a molecule.

Electronegativity of the elements and the type of the bond

A covalent bond is formed due to sharing of an electron pair by two atoms. In a molecule like H₂, in which the atoms are identical, the electrons to be equally attracted by two hydrogen nucleus. However, if we have the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally, because H and F atoms are characterized by different ability to attract electrons. The bond in HF is called a *polar covalent bond*, because the electrons are shifted in the vicinity of the fluorine atom. This "unequal sharing" of the bonding electron pair results in a relatively

greater electron density near the fluorine atom and a correspondingly lower electron density near hydrogen. The HF bond and other polar bonds can be thought of as being intermediate between a nonpolar covalent bond, in which the sharing of electrons is exactly equal, and an ionic bond, in which the transfer of the electrons is nearly complete.

A property of atoms that helps us distinguish a nonpolar covalent bond from a polar covalent bond is *electronegativity*, the ability of an atom to attract toward itself the electrons in a chemical bond. Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity. Thus, an atom such as fluorine, which has a high electron affinity (tends to pick up electrons easily) and a high ionization energy (does not lose electrons easily), has a high electronegativity. On the other hand, sodium has a low electron affinity, a low ionization energy, and a low electronegativity.

Electronegativity is a relative value, showing that an element's electronegativity can be measured only in relation to the electronegativity of other elements. L. Pauling proposed a method for calculating relative electronegativities of most elements. These values are shown in Appendix on the page 46. A careful examination of this table reveals trends and relationships among electronegativity values of different elements. In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each group, electronegativity decreases with increasing atomic number, and increasing metallic character. Note, that the transition metals do not follow these trends. The most electronegative elements – the halogens, oxygen, nitrogen, and sulfur – are placed in the upper right-hand corner of the periodic table, and the least electronegative elements (the alkali and alkaline earth metals) are located near the lower left-hand corner.

Atoms of elements with widely different electronegativities tend to form ionic bonds (such as KCl and CaO, etc.) with each other, because the atom of the less electronegative element gives up its electron(s) to the atom of the more electronegative element. An ionic bond generally joins an atom of a metallic element and an atom of a nonmetallic element. Atoms of elements with comparable electronegativities tend to form polar covalent bonds with each other, because the shift in electron density is relatively small. Most covalent bonds involve atoms of nonmetallic elements. Only atoms of the same elements, which have the same electronegativity, can be joined by a pure covalent bond (non-polar).

There is no sharp distinction between a polar bond and an ionic bond, but the following general rule is helpful in distinguishing between them. An ionic bond forms when the electronegativity difference between the two bonding atoms is 1.7 or more.

LABORATORY EXERCISE No.3.

Preparation of complex compounds

Objective: preparation of the complex compounds of Cu²⁺, Zn²⁺, Cr³⁺, Al³⁺, Fe³⁺ and Ag⁺ ions.

Theoretical background

Complex compounds are compounds with complicated internal structure that produce points (nodes) of the crystal lattices and capable of independent existence in solutions.

According to the A. Werner theory the atoms can exhibit not only a common main valence but also the *complementary* or the *auxiliary* valence. By the Werner auxiliary valences are saturated with the formation of complex compounds. Only negatively charged ions are saturate the main valence of metal cations, but auxiliary valences may be filled by both negatively charged ions and neutral molecules. Each complex has a *central atom* (complexion agent, central ion) around which its coordinated ions and molecules are located. These ions and molecules are called *ligands*. Any complex is characterized by the *coordination number* that shows how many atoms, ions or molecules placed around the central atom. It indicates the total number of σ-type chemical bonds that the central atom forms with the ligands. The coordination number is determined by the nature of the central atom and ligands and can be from 2 to 12. The quantity of the coordination places, which the ligand can occupy, are determined by its *denticity*.

Coordinated through the main and auxiliary valences particles are located in the *internal (inner) sphere* of the coordination compounds. The central atom and the internal sphere form the *complex particle*, which restrict by the square brackets in formulas. The complex particle can be neutral, positively or negatively charged, for example, $[Ni(CO)_4]$, $[Mn(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{3-}$. If the complex particle is charged, than com-

pound has an *external (outer) sphere*, because the every charged ion attracts oppositely charged ions, for example, [Mn(H₂O)₆]Cl₂, K₃[Fe(CN)₆].

Experiments

Formation and investigation of the tetraamminecopper (II) sulphate

Pour 3-4 mL of CuSO₄ solution into a test tube. Add 5 drops of diluted ammonia solution (NH₃·H₂O). Observe precipitation of the copper (II) hydroxide. Then add 4-6 drops of the concentrated ammonia solution. The precipitate of Cu(OH)₂ is dissolved due to formation of tetraamminecopper (II) sulfate. This process is accompanied by the change of solution color. Pour the solution obtained into three test tubes. Leave one test tube as a control. Add 2-3 drops of BaCl₂ solution to the second test tube. Add a tin granule to the third one. What is observed? Repeat the experiments with BaCl₂ and Sn with initial CuSO₄ solution. Note and explain the difference in experiments with metallic tin.

Write the equations of all reactions. Write the formula of the tetraamminecopper (II) sulfate and equation of its electrolytic dissociation, if it is known, that this complex compound dissociates in solution forming two ions.

Formation of the hydroxycomplexes of Zn^{2+} , Cr^{3+} and Al^{3+} ions

Take three test tubes and pour 15 drops of zinc, chromium (III) and aluminium salt solutions. Add dropwise 2-10 drops of concentrated NaOH or KOH solution into each test tube. Observe precipitation of metal hydroxides and their following dissolution in excess of the alkali.

Write the equations of all reactions considering that the obtained soluble hydroxycomplexes contain $[Zn(OH)_4]^{2-}$, $[Cr(OH)_4]^{-}$ and $[Al(OH)_4]^{-}$ ions.

Chelate complex compounds

Pour into three test tubes 3 drops of FeCl₃ solution. Leave one test tube as a control. Into the other two test tubes add 3 drops of NaOH or KOH solution. In the first test tube with the precipitate obtained add 15 drops of oxalic acid $(H_2C_2O_4)$ and to the second one add the same amount of citric acid $(C(OH)(COOH)(CH_2COOH)_2)$.

Structural formulas of oxalic and citric acids

In all three test tubes (including the control test tube) add 2 drops of NH₄CNS or KCNS solution and observe the formation of the brightly colored complex compound.

Write the chemical equations of all reactions.

Complexes in the exchange reactions

Pour into test tube 5 drops of $CuSO_4$ solution. Add the same amount of $K_4[Fe(CN)_6]$ solution. Note the color of the obtained precipitate.

Write the ionic and molecular equations of the reaction.

Destruction of complexes by dilution

- 1) Pour into test tube 2 drops of AgNO₃ solution. Add by dropping the concentrated potassium iodide solution and observe the formation of yellow precipitate of AgI. Then add some amount of KI solution and shake the test tube after each addition till the precipitate dissolves (sometimes the addition of solid KI is needed for dissolution). Why the precipitate was dissolved? Add 5-6 drops of water to the resulting solution, observe changes.
- 2) Pour into test tube 2-3 drops of Bi(NO₃)₃ solution. Add by dropping diluted KI solution and observe changes. Then add concentrated potassium iodide solution and observe dissolution of the precipitate. Why the precipitate of BiI₃ was dissolved? Fill the test tube with water for 2/3 of its volume and wait for 5 minutes. What is observed?

Write the equations of next reactions: formation of the precipitate, its transformation to the complex compound, dissociation of the complex ion. What impact has the dilution of the solution?

Questions for the laboratory exercise No.3

- 1. Which particles can form complex compounds? Are these particles neutral or charged?
- 2. What is the inner and outer sphere of the complex compound?

- 3. What is the difference between ligands and inner sphere of the complex compound?
- 4. Give two examples for the neutral, positively and negatively charged complex particles.
- 5. How to determine the coordination number of the central atom in structure of the complex compound?

Further readings

- 1. Chang R. Chemistry. 10-th edition. NY: McGraw-Hill, 2010. 1170 p.
- 2. Atkins P., de Paola J. Physical Chemistry for the Life Sciences. W.H.Freeman Publishers, 2006. 624 p.

THEME 4. SOLUTIONS. ELECTROLYTIC DISSOCIATION

Many of the reagents used in chemical laboratories are in the form of solutions which need to be purchased or prepared.

Solution is a homogeneous mixture composed of only one phase. In such a mixture, a *solute* is a substance dissolved in another substance, known as a *solvent*. The solvent is commonly the major fraction of the mixture. The solution more or less takes on the characteristics of the solvent including its phase. A solution may be gaseous, solid, or liquid. For medical purposes the most important are liquid solutions, in particularly the aqueous solution in which the solvent is water.

A solution may be more or less concentrated or diluted. This means, it may contain a large or small amount of dissolved substance in a given amount of solvent. Composition of the solution or *concentration* can be expressed in various ways.

The most common unit of solution concentration is *molarity* (M or mol/L). Molarity of a solution is defined as the number of moles of solute per one liter of solution. Note, that the unit of volume for molarity is liter, not milliliter or some other units. Also note, that one liter of solution contains both the solute and the solvent. Molarity, c, therefore, is a ratio of solute moles, n, and volume of solution, V:

$$c = \frac{n}{V} = \frac{m}{M \times V},\tag{4.1}$$

where m is a mass of solute, g; M is a molar mass of solute, g/mol.

The *molality* is another value for the expressing composition of the solutions. It is the number of moles of solute dissolved in 1 kg (1000 g) of a solvent:

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}}, \text{ kg}}.$$
 (4.2)

The unit of molality is mol/kg.

The *mole fraction* of a component of a solution (solute or solvent) is defined as the ratio of the quantity of the component to the quantity of the substance in solution:

$$x = \frac{n_{\text{component}}}{n_{\text{solution}}}.$$
 (4.3)

The mole fraction and the percent by mass (or volume) are unitless values, because they equal to the ratio of two similar quantities.

Mass percent (w) of solute in solution is defined as ratio between mass of a solute and mass of solution

$$w = \frac{m(\text{solute})}{m(\text{solution})} \times 100\% = \frac{m(\text{solute})}{m(\text{solute}) + m(\text{solvent})} \times 100\%. \tag{4.4}$$

This value is equal the grams of solute per 100 grams of solution. For example: 20 g of sodium chloride in 100 g of solution is a 20% by mass solution.

 $\textit{Volume percent }(\phi)$ of a component in solution is defined by the equation

$$\varphi = \frac{V(\text{solute})}{V(\text{solution})} \times 100\%. \tag{4.5}$$

The ϕ value may be considered as the number of the solute milliliters per 100 mL of solution. For example: 10 mL of ethyl alcohol plus 90 mL of water gives approximately 100 mL of solution which contains 10% of ethanol by volume.

Another ways of expressing the solution composition can also be used. One of sometimes used way of expressing the concentration is *titer* concentration, *T*, which shows mass of solute per 1 mL of solution, g/mL.

All solutes, that dissolve in water, can be divided in two categories: *electrolytes* and *nonelectrolytes*. An electrolyte is a substance that, when dissolved in water, results in a solution that can conduct electricity. A nonelectrolyte solution does not conduct electricity. For the explanation of this and some other properties of solutions Swedish scientist S. Arrhenius proposed the *electrolytic dissociation theory*. According to this theory molecules of acids, bases or salts undergo dissociation into ions on dissolution in water. The result of this process is the presence of ions in solution. Positively charged ions are called "cation", negatively charged – "anions".

It was found that sometimes only a part of dissolved molecules undergo dissociation. Fraction of the solute molecules, which is dissociated into ions, is called the *degree of dissociation*. It equals to the number of dissociated molecules (N) divided to the total number of dissolved molecules in solution (N_o) :

$$\alpha = N / N_o. \tag{4.6}$$

Compounds, that completely dissociate, is characterized by $\alpha = 1$ and is called *strong* electrolytes. If the degree of dissociation α is less than 0.03 the electrolyte is called *weak* electrolyte. Electrolyte that characterized by $0.03 < \alpha < 0.30$ is *medium* electrolyte. Degree of dissociation depends on electrolyte concentration and usually decreases with increase in concentration.

In a solution of any electrolyte there is an equilibrium between the free ions, on the one hand, and undissociated molecules, on the other hand, one may write this equilibrium in the form

$$CatAn \rightleftharpoons Cat^+ + An^-$$
,

where Cat⁺, An⁻ – cation and anion of the electrolyte. Mass action law for this equilibrium process gives

$$K = \frac{[\operatorname{Cat}^{+}][\operatorname{An}^{-}]}{[\operatorname{CatAn}]},$$
(4.7)

where [...] – denotes equilibrium concentration of a particle, K – equilibrium constant, called the *dissociation constant*.

It may be shown that for a weak binary electrolyte, e.g. acetic acid, dissociation constant and degree of dissociation interconnected by the expression

$$K = \frac{\alpha^2 c}{1 - \alpha},\tag{4.8}$$

where c – total molar concentration of electrolyte in solution. This equation is known as *Ostwald's dilution law*, it is applicable for weak electrolytes only.

LABORATORY EXERCISE NO.4.

Preparation of solutions and acid-base titration

Objectives: study the experimental techniques of solution preparation (starting from solid substance and from concentrated solution); study the experimental techniques of titration; prepare salt and acid solutions and determine preciously the concentration of acid solution using titration techniques.

Theoretical background

To prepare solutions, usually a given volume and molarity are required. To determine molarity, the molar mass of the solute is needed. The following examples illustrate the calculations for preparing solutions.

If starting with a solid, use the following procedure:

- Determine the mass in grams of one mole of solute, the molar mass, *M*.
 - Decide volume of solution required, in liters, V.
 - Decide molarity of solution required, c.
- Calculate mass of solute (m) required using equation (4.9), derived from equation (4.1):

$$m = c \times M \times V. \tag{4.9}$$

Example: Prepare 800 mL of 2 M sodium chloride.

M(NaCl) = 58.45 g/mol,

 $m(NaCl) = 58.45 \text{ g/mol} \times 2 \text{ mol/L} \times 0.8 \text{ L},$

m(NaCl) = 93.52 g NaCl.

Dissolve 93.52 g of NaCl in about 400 mL of distilled water, then add more water until final volume is 800 mL.

If starting with a solution or liquid reagent:

- When diluting more concentrated solutions, decide what volume (V_2) and molarity (c_2) of the final solution should be. Volume can be expressed in liters or milliliters.
 - Determine molarity (c_1) of starting, more concentrated solution.
- Calculate volume of starting solution (V_1) using equation (4.10), note: V_1 must be in the same units as V_2 :

$$c_1 \times V_1 = c_2 \times V_2 \,. \tag{4.10}$$

Example: Prepare 100 mL of 1.0 M hydrochloric acid from concentrated (12.1 M) hydrochloric acid.

$$c_1 \times V_1 = c_2 \times V_2,$$

$$(12.1 \text{ M}) \times (V_1) = (1.0 \text{ M}) \times (100 \text{ mL}).$$

 $V_1 = 8.26 \text{ mL}$ of concentrated HCl solution.

Add 8.26 mL of concentrated HCl to about 50 mL of distilled water, stir, then add water up to 100 mL.

To prepare a mass percent solution starting with a solid use the following procedure:

- Determine the mass percent concentration of solution, w, and the mass of solution in grams, m(solution).
- Calculate the mass of solute using equation (4.11), derived from equation (4.4):

$$m(\text{solute}) = \frac{w \times m(\text{solution})}{100\%}$$
 (4.11)

• Calculate the mass of solvent as a difference between solution mass and solute mass:

$$m(\text{solvent}) = m(\text{solution}) - m(\text{solute}).$$
 (4.12)

• Solvent can be added by volume. For this purpose use the graduated cylinder and equation (4.13), which connects the volume and mass of liquid throw its density, d:

$$m(\text{solvent}) = d(\text{solvent}) \times V(\text{solvent}).$$
 (4.13)

Example: Prepare 100 g of 5 % potassium chloride solution in water.

 $m(\text{solute}) = w \times m(\text{solution})/100\%,$

$$m(KC1) = (5 \%) \times (100 g) / 100 \% = 5 g,$$

$$m(\text{water}) = 100 \text{ g} - 5 \text{ g} = 95 \text{ g}.$$

As the density of water is approximately equal 1 g/mL, 95 g of water makes 95 mL.

Measure 95 mL of water, add 5 g of KCl to about 50 mL of distilled water, stir, then add the rest of water.

For many purposes, the exact value of concentration is not critical; in other cases, the concentration of the solution and its method of preparation must be as accurate as possible. Establishing the composition of the solu-

tion is one of the most important tasks of chemistry. Quantitative analysis can be performed by physical, chemical and physico-chemical methods. One of the most common among them is *titrimetry*.

In a *titration*, a solution of accurately known concentration, called a *standard solution* or *titrant*, is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Titration is the most convenient technique used to carry out quantitative studies of acid-base (neutralization) reactions, for example,

$$HCl + NaOH \Rightarrow H_2O + NaCl.$$

In general such reactions may be written in form

$$H^+ + OH^- \rightleftharpoons H_2O$$
.

For example, when an acid is titrated with a standard solution of base, the *equivalence point* is reached when all of the acid has been neutralized by the base. At this point, the moles of base that have been added is equal to the number of moles of acid that were in the sample.

Since we cannot actually watch the molecules react, we do not know exactly when the equivalence point occurs. We can approximate the equivalence point by observing the *end point* – the point at which the color of an indicator is changed.

An *acid-base indicator* is a substance that changes color with the pH value of solution. Usually it is a weak acid that is one color when protonated and another color when deprotonated. At low pH, the protonated form dominates, whereas at high pH the excess of hydroxide ion (OH⁻) in solution causes the indicator to become deprotonated and thereby change color.

$$HIn(color 1) + OH^- \rightleftharpoons In^-(color 2) + H_2O.$$

In the titration of an acid with a base, just after the equivalence point is reached there is suddenly an excess of hydroxide ion in solution. This excess hydroxide ion deprotonates the indicator and a sudden color change is observed, signaling the end point.

A sudden color change due to the indicator signals that neutralization has occurred. At this point, the number of hydrogen ions (H⁺) from the acid is equal to the number of hydroxide (OH⁻) ions from the base. When the

end point is reached, the volume of the standard solution is carefully determined. Then the measured volumes of the two solutions and the known concentration of the standard solution are used to calculate the concentration of the other solution.

The change of indicator color is occurred in the definite range of the pH values. This interval of the pH is called *the transition or useful range of the indicator*. Commonly used organic dyes, whose color changes on changing in pH value of solution are shown in Table 1.

	\mathcal{E}	1
Indicator	Color change region, pH	Change of colors
Phenolphthalein	8.2-10.0	colorless to pink
Litmus	5.0-8.0	red to blue
Methyl orange	3.0-4.4	red to orange
Methyl red	4.4-6.2	red to yellow

Table 1. Colors and useful ranges for some pH indicators

Indication of color change in solutions can be carried out both visually and by instrumental techniques. In case when sample or titrant is colored itself, special indicators may not be necessary.

Concentration of a solute in the sample solution can be determined according to equation

$$c_{\text{H}^+} \times V_{\text{H}^+} = c_{\text{OH}^-} \times V_{\text{OH}^-},$$
 (4.14)

where $c_{\rm H}^{+}$ and $c_{\rm OH}^{-}$ are concentrations of hydrogen and hydroxide ions in sample and titrant respectively, $V_{\rm H}^{+}$ and $V_{\rm OH}^{-}$ are volumes of sample and titrant, spent on neutralization of the sample, respectively.

Knowing three of these quantities from the performed titration procedure we can calculate the concentration in the sample.

Experiments and calculations

The volumetric pipet and buret are fragile and expensive. Treat them with care.

Task 1. Prepare 0.9 mas. % sodium chloride solution (saline solution) of certain mass

Ask the teacher for the mass of solution.

Calculate the mass of NaCl required for solution using equation (4.11).

Weight the calculated amount of NaCl using the most accurate balance available for you.

Using a funnel place weighted NaCl in a clean flask.

Assuming that density of distilled water at room temperature equals 1 g/mL, calculate the volume of water to be add to a solution using equation (4.12).

Measure the required volume of distilled water using a graduated cylinder.

Add about half of volume of water to a flask with salt, washing into the flask any salt crystals clinging to the funnel. Remove funnel and gently swirl the flask to dissolve the salt. When the salt is dissolved, add the rest of water from cylinder.

Task 2. Prepare 0.1 mol/L acetic acid solution in water by diluting of a concentrated solution

Ask the teacher for the volume of solution to prepare and for the concentration of starting solution.

Check the molarity of starting solution (c_1) , molarity and volume of final solution (c_2, V_2) and using equation (4.10) determine the volume of starting solution (V_1) .

Get a clean volumetric flask of required volume, pipet, pipet pump.

Fill volumetric flask 1/2-1/3 full with distilled water.

Pipet V_1 of concentrated acetic acid solution using a pipet pump, place it to the volumetric flask. Handle the concentrated acetic acid with care. It can cause painful burns if it comes in contact with the skin!

Stir the flask for a while carefully; add distilled water up to mark.

Task 3. Determine the exact concentration of acetic acid solution, obtained in Task 2.

Get a clean pipet of 5 or 10 mL (ask a teacher), pipet pump, and 3 flasks.

Rinse your pipet with 2-3 mL of prepared in Task 2 solution of acetic acid several times.

Using a pipet and pipet pump place an equal samples of prepared in Task 2 solution to each of flasks, add to each of them approximately 100 mL of distilled water and 2-3 drops of solution of phenolphthalein as indicator.

Fill a clean buret with a solution of NaOH of known concentration to the top of the graduated portion and make sure that the buret tip is full of solution. With a piece of filter paper remove any drop of NaOH hanging from the tip.

Make a titration of each solution in flask. While making a titration, place a sheet of white paper under the flask so that the color of the solution is easily observed. Read and record the position on the buret of the lowest point of the meniscus of NaOH solution. Swirl the flask and add NaOH solution. Titrate until the last drop of NaOH solution leaves a permanent pink color in the solution.

No drop should be left hanging on the buret tip. Read and record the level of the meniscus in the buret, and calculate the volume of basic solution used in the titration.

Now titrate others two samples of acid solution prepared in Task 2, being certain that the buret is refilled nearly to the top of the graduated portion with NaOH solution and that you use a clean flask. In this and subsequent runs you may add NaOH solution from the buret very rapidly up to about 2 mL less of the volume you estimate on the basis of your first titration. Then carefully add the rest of the base drop by drop so that you can determine the endpoint accurately.

After performing 3 titrations make sure, that volumes of standard solution used for each titration, are in agreement within \pm 0.3 mL.

Fill the following table with results of measurements:

Sample number	Volume of NaOH used, mL	Concentration of acetic acid, mol/L	Average concentration of acetic acid, mol/L
1.			
2.			
3.			

Determine the concentration of acetic acid solution using equation (4.15), and write these values to the table above

$$c_{HAc} = \frac{c_{NaOH} \times V_{NaOH}}{V_{HAc}}.$$
 (4.15)

Also calculate the average concentration of acetic acid and write this value to the table.

Questions for the laboratory exercise No.4

- 1. Define the following terms: solution, solvent, solute.
- 2. What expression of solution composition do you know?
- 3. What is titrimetry? What is the main principle of titrimetry? Write down the main equation for the determination of concentration in titrimetry.
- 4. On which property of indicators their application is based?
- 5. Discuss the titration process was your titration successful? Why yes or why not?
- 6. The concentration of the acetic acid solution prepared in Task 2 can be easily calculated using the $c_1 \times V_1 = c_2 \times V_2$ equation, so what was the reason for performing the titration procedure?

LABORATORY EXERCISE NO.5.

Determination of the pH value of solutions by indicator method

Objective: Investigation of acidity (alkalinity) of solutions using acid-base indicators.

Theoretical background

Water molecules exist in equilibrium with hydrogen ions and hydroxide ions

$$H_2O \rightleftharpoons H^+ + OH^-$$
.

The water equilibrium constant is written as:

$$K_w = [H^+][OH^-].$$
 (4.16)

It has been found experimentally that the concentrations of hydrogen and hydroxyl ions in pure water are equal:

$$[H^+] = [OH^-] = 10^{-7} \text{ mol/L}.$$

Therefore

$$K_w = 10^{-7} \times 10^{-7} = 10^{-14}$$
. (4.17)

In other words, only very small amounts of H⁺ and OH⁻ ions present in pure water and their concentrations are interconnected. If an acid is added to the water, the equilibrium of water dissociation shifts to the left and the OH⁻ ion concentration decreases. If base is added to water, the equilibrium shifts to the left too, but in this case the H⁺ concentration decreases.

Constant K_w is known as *ionic product of water*. At 25 °C the K_w value is equal to $1.008 \cdot 10^{-14}$. Usually this constant is represented as the negative decimal logarithm:

$$pK_w = -\log K_w$$
; $pK_w = 14$ at 25 °C.

The *pH value of a solution* is defined as the negative decimal logarithm of the hydrogen ion concentration

$$pH = -log[H^{+}].$$
 (4.18)

Similarly for hydrogen ion concentration

$$pOH = -log[OH^{-}]. \tag{4.19}$$

It is obvious that

$$pOH + pH = pK_w = 14.$$
 (4.20)

The pH and pOH values of diluted solutions are in range 0–14. But concentrated solutions of a strong acids may have zero or even negative pH values, and concentrated solutions of a strong bases may have pH values more than 14.

Hydrolysis is the cleavage of chemical bonds by the addition of water. Generally, hydrolysis is a process of chemical interaction between water and a substance.

A common kind of hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water spontaneously ion-

izes into hydroxyl anions and hydrogen cations. The salt, too, dissociates into its constituent anions and cations. For example, sodium acetate dissociates in water giving sodium and acetate ions

$$CH_3COONa + H_2O \Rightarrow CH_3COOH + Na^+ + OH^-.$$

The acetate ions combine with hydrogen ions to produce molecules of acetic acid, but sodium cations and hydroxyl anions do not react, because NaOH is a strong electrolyte and exists in solution in dissociated state. In this case, the net result is a relative excess of hydroxyl ions, giving a basic solution.

Read about acid-base indicators in theoretical background for laboratory exercise No.4.

Experiments

Color of indicators

Into three test tubes pour solutions of hydrochloric acid (to the first test tube), sodium hydroxide (to the second test tube) and distilled water (to the third one). Add one drop of methyl orange solution to each test tube. Observe color changes of the indicator in all solutions.

Pour to test tubes 4-5 different buffer solutions with known pH values and add a drop of universal indicator solution to each of them. State the pH of the solutions using scale for universal indicator. Compare stated and initial pH values.

Influence of hydrolysis on pH value of solutions

Use water solutions of NaCl, NaHCO₃, Na₂CO₃, CH₃COONa, ZnCl₂ and NH₄Cl. Determine pH values of the solutions using indicator paper.

Determine the pH value of distilled water and tap water. Compare these results.

Explain the pH values obtained for each solution.

Comparison of hydrolysis degree

Determine and compare the pH values of aluminium sulphate and magnesium sulphate aqueous solutions using indicator paper.

In the same way determine and compare pH of sodium sulphite and sodium carbonate aqueous solutions.

Explain the differences in pH values of these solutions using data for electrolyte power:

- H₂SO₄ and NaOH are strong electrolytes to be fully dissociated;
- H₂SO₃ and H₂CO₃ are weak acids and the first is stronger;
- Mg(OH)₂ and Al(OH)₃ are weak bases and the second is weaker.

Temperature influence on hydrolysis

Add two spatula of sodium acetate into a test tube. Dissolve the salt in 2 ml of water and add 1-2 drops of phenolphthalein solution to furnish light pink color. Then heat the test tube in a beaker filled with hot water. Observe and explain changes in solution's color.

Questions for the laboratory exercise No.5

- 1. Which type of chemical compounds belongs to acid-base indicators?
 - 2. What are pH and pOH values of a solution?
 - 3. What is hydrolysis?
 - 4. In which cases hydrolysis of inorganic salts occurs?
- 5. Why the pH scale in diluted aqueous solutions is limited in range 0–14? Is pH scale different in ethanol solutions?

Further readings

- 1. Chang R. Chemistry. 10-th edition. NY: McGraw-Hill, 2010. 1170 p.
- 2. Atkins P., de Paola J. Physical Chemistry for the Life Sciences. W.H.Freeman Publishers, 2006. 624 p.
- 3. Allen J.P. Biophysical Chemistry. Blackwell Publishing, 2008. 492 p.

THEME 5. COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative properties of solutions are several important properties that depend on the number of solute particles in solution and not on the nature of the solute particles. These particles may be atoms, ions or molecules. It is important to keep in mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations are less than 0.1 mol/L. The term "colligative properties" denotes "properties that depend on the collection".

The colligative properties are:

- vapor pressure lowering,
- boiling-point elevation,
- freezing-point depression,
- osmotic pressure.

Vapor pressure lowering

Vapor pressure of a liquid substance is the pressure due to molecules of this substance that would be generated if the gas and the liquid phases of the substance were allowed to reach equilibrium in a closed system.

If a solute is *nonvolatile* (this means, it has a very low, unmeasurable vapor pressure), vapor pressure of the solution is always less than that of the pure solvent and depends on the concentration of the solute. The relationship between solution vapor pressure and solvent vapor pressure was obtained by French chemist Francois Raoult and is known as *Raoult's law*. This law states that *the vapor pressure of a solvent over a solution* (p_1) *equals the product of vapor pressure of the pure solvent* (p_1°) *and the mole fraction of the solvent in the solution* (x_1) :

$$p_1 = x_1 p_1^{\circ}. (5.1)$$

In a solution containing only one solute, than $x_1 = 1 - x_2$, where x_2 is the mole fraction of the solute. Equation of the Raoult's law can therefore be rewritten as

$$(p_1^{\circ} - p_1)/p_1^{\circ} = x_2. \tag{5.2}$$

One can see that the relative decrease in vapor pressure of the solvent is directly proportional to the mole fraction of the solute in solution.

If both components of a solution are *volatile* and characterized by measurable vapor pressure, the vapor pressure of the solution is the sum of the individual partial pressures. In this case Raoult's law holds equally for all components:

$$p_i = x_i p_i^{\circ}. \tag{5.3}$$

Elevation of boiling point

Because the presence of a solute lowers the vapor pressure of a solvent over the solution, it must also affect the boiling point of the solution. The boiling of a pure liquid or a solution occurs at that temperature at which its vapor pressure becomes equal the external atmospheric pressure. Because at any temperature the vapor pressure of the solution is lower than that of the pure solvent, the vapor pressure of solution reaches atmospheric pressure at a *higher* temperature than the normal boiling point of the pure solvent. This leads to *elevation of boiling point* of solution in comparison with pure solvent. The boiling-point elevation is defined as

$$\Delta T_b = T_b - T_{b,o} > 0, (5.4)$$

where T_b is the boiling point of the solution and $T_{b,o}$ – the boiling point of the pure solvent. Because ΔT_b is proportional to the lowering of the vapor pressure, it must be also proportional to the concentration of the solution. It has been found experimentally that

$$\Delta T_b = K_b m, \tag{5.5}$$

where m is the molality of the solution and K_b is the molal boiling-point elevation constant. The units of K_b are $K \cdot kg \cdot mol^{-1}$.

It has been proved theoretically that K_b is determined only by properties of the solvent:

$$K_b = \frac{RT_{b,o}^2 \cdot M_1}{1000 \cdot \Delta H_{vap}^o},$$
 (5.6)

here R – universal gas constant, M_1 – molar mass of the solvent, ΔH_{vap}^o – enthalpy change of vaporization of the pure solvent.

The value of boiling-point elevation constant for water is $0.52 \, \text{K} \cdot \text{kg} \cdot \text{mol}^{-1}$, one can see that if the molality of an aqueous solution is $1.00 \, \text{mol/kg}$, the boiling point will be $100.52 \, ^{\circ}\text{C}$.

Depression of freezing point

The phenomenon of the depression of the freezing point of a solution is caused by the lowering the vapor pressure of the solution like elevation of boiling point. The pure solvent freezes if its vapor pressures in liquid and solid states are equal. The vapor pressure of a solid solvent depends on temperature only and decreases with the decrease in temperature. This leads the temperature of the freezing of solution is *lower* than the freezing point of the solvent. The *depression of freezing point* is defined as

$$\Delta T_f = T_{o,f} - T_f > 0, (5.7)$$

in which $T_{o,f}$ is the freezing point of pure solvent, and T_f – the freezing point of the solution. The ΔT_f value is proportional to the molal concentration of the solute:

$$\Delta T_f = K_f m, \tag{5.8}$$

in which m is the solute molality, and K_f is the molal freezing-point depression constant. Like K_b , the K_f has the units of $K \cdot kg \cdot mol^{-1}$ and depends only on properties of the solvent:

$$K_f = \frac{RT_{f,o}^2 \cdot M_1}{1000 \cdot \Delta H_{fus}^o},\tag{5.9}$$

where ΔH_{fus}^{o} is enthalpy change of fusion of the pure solvent.

The value of freezing-point depression constant for water is $1.86 \text{ K}\cdot\text{kg}\cdot\text{mol}^{-1}$, one can see that if the molality of an aqueous solution is 1.00 mol/kg, the freezing point will be $-1.86 \,^{\circ}\text{C}$.

Osmosis

The phenomenon of osmosis is the spontaneous movement of a pure solvent into a solution separated from it by a semipermeable membrane.

The membrane is permeable only by the solvent molecules but not by the solute and allows the solvent to pass through. The word *osmosis* originates from the Greek word meaning "push".

The osmotic pressure is the pressure that must be applied to the solution to prevent the solvent transfer.

For dilute solutions the osmotic pressure is given by the van't Hoff's equation:

$$\pi = cRT \,, \tag{5.10}$$

where T – absolute temperature, c – molar concentration of the solute. If universal gas constant is used as 8.314 J/(mol·K), and molar concentration is expressed in units of mol/m³, then osmotic pressure is expressed in Pascals.

If two solutions are of equal concentration and, hence, of the same osmotic pressure, they are said to be *isotonic*. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be *hypertonic* and the more dilute solution is described as *hypotonic*.

Colligative properties of electrolyte solutions

Colligative properties of electrolytes is characterized by slightly different approach than the one used for the colligative properties of nonelectrolytes. The reason is that electrolytes dissociate into ions in solution, and so one unit of an electrolyte compound separates into two or more particles when it dissolves.

Thus, the colligative properties of binary electrolyte solution should be twice as great as those of an electrolyte solution containing a nonelectrolyte in the same concentration. Similarly, we would expect a ternary electrolyte solution to depress the freezing point by three times as much as a nonelectrolyte solution with the concentration. To account for this effects we must modify the equations for colligative properties as follows:

$$(p_1^{\circ} - p_1)/p_1^{\circ} = ix_2, \tag{5.11}$$

$$\Delta T_b = iK_b \cdot m, \tag{5.12}$$

$$\Delta T_f = iK_f m, \tag{5.13}$$

$$\pi = icRT. \tag{5.14}$$

The variable *i* is the *van't Hoff's isotonic factor*, which is defined as the ratio of actual number of particles in solution after dissociation and number of molecules (structural units) of initially dissolved substance.

Thus, *i* should be 1 for nonelectrolytes. For strong binary electrolytes such as NaCl and KNO₃, should be 2, and for strong ternary electrolytes such as Na₂SO₄ and MgCl₂, *i* should be 3. In reality, the colligative properties of electrolyte solutions are usually smaller than anticipated, because at higher concentrations, electrostatic forces come into play, drawing cations and anions together. A cation and an anion held together by electrostatic forces is called an ion pair. The formation of an ion pair reduces the number of particles in solution by one, causing a reduction in the colligative property.

Review questions for the theme 5

- 1. What are colligative properties of solutions? What is the meaning of the word "colligative" in this context?
 - 2. Write the equation of Raoult's law and express it in words.
- 3. Write the equations for interconnection between boiling-point elevation and freezing-point depression and the concentration of the solution.
- 4. What is osmosis? What is a semipermeable membrane? Write the equation relating osmotic pressure to the concentration of a solution, specify the units for all values.
 - 5. What is the van't Hoff's isotonic factor?

Further readings

- 1. Chang R. Chemistry. 10-th edition. NY: McGraw-Hill, 2010. 1170 p.
- 2. Atkins P., de Paola J. Physical Chemistry for the Life Sciences. W.H.Freeman Publishers, 2006. 624 p.
- 3. Allen J.P. Biophysical Chemistry. Blackwell Publishing, 2008. 492 p.

SAFETY RULES IN CHEMICAL LABORATORY

A. Rules governing personal safety

You may be dismissed permanently from the laboratory for violating any of the following rules:

- 1. No eating, drinking or smoking in the laboratory. Chemicals could accidentally be ingested with food or drink. In addition to promoting many kinds of cancer, smoking is hazardous because many chemicals are flammable. Do not bring any food, beverages, or food containers into lab.
- 2. Perform only authorized experiments. While working with chemicals and devices do not deviate from the instructions. One should give attention while mixing chemicals. Do not mix them randomly otherwise it could result in serious consequences.
- 3. Use appropriate lab coat. Clothing that provides complete leg coverage (such as jeans or long skirts) is required. Absolutely no shorts, miniskirts, or halter-tops will be allowed in lab! Some chemicals can damage clothes and can leave permanent stains. Wear shoes that provide complete foot coverage to protect your feet from both spilled chemicals and broken glassware. Note: should you come to lab inappropriately dressed, you will be dismissed from lab to change into appropriate attire.
- 4. Eye goggles that completely cover the eyes must be worn at all times in the laboratory while doing an dangerous experiment to guard against potential eye injury.
- 5. Do not taste or sniff chemicals. For many chemicals, if you can smell them then you are exposing yourself to a dose that can harm you! If the safety information says that a chemical should only be used inside a fume hood, then do not use it anywhere else. This is not cooking class do not taste your experiments!
 - 6. Do not pipette by mouth.
 - 7. Wash hands before leaving lab.

B. Guidelines for personal safety

1. Keep your lab area and equipment clean. By eliminating unnecessary clutter, accidents can be prevented. Your lab area includes your sink. Do not throw paper products or other solids in the sink. Proper disposal containers are available. Dirt or chemical residues in the equipment may

interfere with your experimental reactions and make lab interpretation more difficult (if not impossible!). Chemicals often corrode metal equipment. Keeping the lab clean and safe is everyone's responsibility!

- 2. Avoid rubbing your eyes while in lab. You may accidentally transfer chemicals to your eyes and cause damage to them. When goggles get foggy and/or your eyes need attention, wash your hands well before going out into the hall to take care of the problem.
- 3. Secure (tie back) long hair. Hair can catch fire, get caught in equipment, or be damaged by chemicals if not secured.
- 4. Avoid direct contact with the reagent chemicals. Contact may adversely affect your skin and experimental results. Many chemicals will burn or irritate skin. If you spill a chemical on your skin, flush it with water immediately and then wash with soap and water. Treat all chemicals as potentially dangerous.
- 5. Wash your hands before leaving lab. Certain chemicals do not burn or stain the instant they come in contact with your skin, but they may after they have been there for a while. The possibility also exists for contaminating other things you come in contact with after you leave lab (such as your belongings, food and drink, etc.). In the case of an accident or emergency, the following points of discussion may completely escape your recollection. Most people when surprised or frightened display a reaction noticeable to those around them. This is good! Just as promoting safety and preventing accidents is everyone's business, so is the patching up of any disaster. Keep alert so that if a problem arises you can properly respond to it. Please help whenever possible.

C. In the case of an accident

In the case of an accident or emergency, consider the following.

- 1. Immediately indicate the need for help whether you are the victim or the observer. A gasp, scream, or shout is appropriate. If you are a bystander, notify the instructor, laboratory assistant or stockroom personnel of the accident or emergency.
- 2. In order to deal with eye injury, chemical spills or fire, know the location and use of: the eyewash, safety shower, the fire extinguishers, the fire blanket and first aid kit.

- 3. If a corrosive chemical gets on your skin, clothing or in your eyes, immediately wash the affected area with large quantities of water. Use the eyewash or safety shower if the situation calls for it. Remove clothing if necessary in the case of either a spill or fire.
- 4. If you spill a chemical, clean it up as directed by your instructor, lab assistant or stockroom personnel. If it is a spill that might endanger your neighbors, alert them to the problem.
- 5. Small-contained fires can be extinguished by covering them with a beaker or even a wet paper towel. For an open fire, use the fire extinguisher. Be sure to point it at the base of the flame.
- 6. No matter how small the injury or accident, please notify your instructor. An accident report must be filed for all injuries sustained in the laboratory.
 - 7. If additional medical attention is necessary call 103.

D. Good laboratory practices

- 1. Treat all lab equipment as sacred. Some equipment is quite expensive and delicate (e.g., the balances), and often critical in obtaining easily interpreted results. Consult the techniques section or the common laboratory techniques section of the manual.
- 2. Read the reagent bottle twice before using the chemical from it to promote safety and to avoid errors which may require repeating the experiment.
- 3. Always clean glassware before and after using it. The glassware is shared among many students.
- 4. Never heat a closed system. Excess pressure builds up that could easily cause an explosion.
- 5. When heating a test tube, point the open end toward an unoccupied area, preferably at a wall. The same applies for stoppered test tubes.
- 6. Add reagents slowly and carefully. Pour concentrated solutions into water or less concentrated (dilute) solutions in order to avoid violent, uncontrolled reactions. For example, when acid and water are mixed, pour the acid into the water.
- 7. When determining the odor of chemicals, smell them indirectly by waving your hand over the top of the container and fanning the odor toward your nose.

- 8. Perform reactions with smelly, noxious, or dangerous chemicals in a fume hood.
- 9. Proper laboratory technique demands that you do not leave the laboratory without cleaning it. As a general rule, the lab should look as good if not better than when you walked in. This includes:
 - cleaning your work area;
 - straightening chemicals;
 - put to rights balances and devices;
 - putting paper and other refuse in the garbage can.

Further readings

- 1. Chemical safety for teachers and their supervisors. Washington: ACS Publications, 2001. 24 p.
- 2. Chemical safety manual for small businesses. guides for managers, administrators, and employees. Washington: ACS Publications, 2009. 90 p.
- 3. Furr A.K. CRC Handbook of laboratory safety. Boca Raton: CRC Press, 2000.

APPENDIX

Table 1. Fundamental constants

Quantity	Symbol	Value	Power of ten	Units			
Speed of light	С	2.99792458 (exact value)	10 ⁸	$\mathbf{m} \cdot \mathbf{s}^{-1}$			
Elementary charge	e	1.602176	10^{-19}	C			
Avogadro's constant	N_A	6.02214	10^{23}	mol ⁻¹			
Faraday constant	$F = N_A e$	9.6485	10 ⁴	C·mol ^{−1}			
Boltzmann constant	k	1.38065	10^{-23}	$J \cdot K^{-1}$			
Gas constant	$R=N_A k$	8.31447 8.20574	$\frac{-}{10^{-2}}$	$J \cdot K^{-1} \cdot mol^{-1}$ $L \cdot atm \cdot K^{-1} \cdot mol$			
Planck's constant	h	6.62607	10^{-34}	$J \cdot s$			
Atomic mass unit	u	1.66054	10^{-27}	kg			
Mass							
electron	m_e	9.10938	10^{-31}	kg			
proton	m_p	1.67262	10^{-27}	kg			
neutron	m_n	1.67493	10^{-27}	$\frac{\text{kg}}{\text{J}^{-1} \cdot \text{C}^2 \cdot \text{m}^{-1}}$			
Vacuum permittiv-	ϵ_0	8.85419	10^{-12}	$J^{-1} \cdot C^2 \cdot m^{-1}$			
ity	$4\pi\epsilon_0$	1.11265	10^{-10}	$J^{-1} \cdot C^2 \cdot m^{-1}$			
Standard accelera-	a	9.80665		$\mathrm{m}{\cdot}\mathrm{s}^{-2}$			
tion of free fall	g	(exact value)	<u>-</u>	111.2			
Gravitational constant	G	6.674	10^{-11}	N⋅m²⋅kg ⁻²			

Table 2. The most abundant elements in the Earth's crust and human body

Human boo	dy	Earth's crust				
Element	Percentage (by weight)	Element	Percentage (by weight)			
Oxygen	65	Oxygen	46.6			
Carbon	18	Silicon	27.7			
Hydrogen	9.5	Aluminium	8.1			
Nitrogen	3.3	Iron	5.0			
Calcium	1.5	Calcium	3.6			
Phosphus	1	Sodium	2.8			
Sulfur, sodium, po- tassium, chlorine	0.2	Potassium	2.6			
Magnesium	0.05	Magnesium	2.1			
Iron, fluorine	0.005	Hydrogen	0.14			
Zinc	0.003	Phosphus	0.07			
Copper, bromine	2.10-4	Carbon	0.03			
Selenium, manga- nese, arsenic, nickel	2.10-5	Sulfur	0.03			
Lead, cobalt	9.10 ⁻⁶	Chlorine	0.01			

The Greek alphabet

Letter	Name	Letter	Name
Α, α	alpha	N, v	nu
Β, β	beta	Ξ, ξ	xi
Γ, γ	gamma	0 0	omicron
Δ, δ	delta	Π,π	pi
Ε, ε	epsilon	P, p	rho
Z, ζ	zeta	Σ, σ	sigma
Η, η	eta	Τ, τ	tau
Θ, θ	theta	Υ, ε	upsilon
I, t	iota	Φ, φ	phi
Κ, κ	kappa	X, χ	chi
Λ, λ	lambda	Ψ, ψ	psi
Μ, μ	mu	Ω, ω	omega

2 Te	helium 4.003	10	Ne	neon	20.18	18	Ā	argon 39.95	36	۲	krypton 83.80	54	Xe	xenon	98	Ru	radon										
	17	6	ш	fluorine	19.00	17	రె	chlorine [35.44; 35.46]	35	Ā	bromine 79.90	53	_	iodine	85	Ąţ	astatine					71	Ľ	lutetium 175.0	100	20 1	LF
	16	8	0	oxygen	[15.99; 16.00]	16	ဟ	.08]	34	Se	selenium 78.96(3)	52	Те	tellurium	84	Ро	polonium					70	γ	ytterbium 173.1	100	701	nobelium
	15	7	z	nitrogen	[14.00; 14.01]	15	۵	phosphorus 30.97	33	As	arsenic 74.92	51	Sb	antimony	83	<u>B</u>	bismuth					69	T	thulium 168.9	707	7	mendelevium
	14	9	ပ	carbon	[12.00; 12.02]	14	S	silicon [28.08; 28.09]	32	Ge	germanium 72.63	50	Sn	tin 118 7	82	Pb	lead					89	ш	erbium 167.3	100	3 L	fermium
W	13	5	В	boron	[10.80; 10.83]	13	₹	aluminium 26.98	31	Ga	gallium 69.72	49	므	indium 111 B	81	F	thallium					29		holmium 164.9		66 L	ES einsteinium
UPAC Periodic Table of the Elements								12	30	Zn	zinc 65.38(2)	48	ဦ	cadmium	80	H	mercury	112		copernicium		99	٥	dysprosium 162.5	00	_ه ځ	californium
the Ek								1	59	Cn	copper 63.55	47	Ag	silver	62	Au	blog 0.791	111	Rg			65	Q T	terbium 158.9	70)	berkelium
ole of								10	28	Z	nickel 58.69	46	Pd	palladium	78	4	platinum	110	Ds	darmstadtium		64	р В	gadolinium 157.3	90	ه ر د	curium
dic Tat								6	27	ပိ	cobalt 58.93	45	格	rhodium	77	_	iridium 1922	109	Μ̈́	meitnerium		63	ш	europium 152.0	90	ce <	americium
Perio								80	26	Fe	iron 55.85	44	Ru	ruthenium	92	Os	osmium 190.2	108	Hs	hassium		62	Sm	samarium 150.4	70	<u></u>	plutonium
IUPAC								7	25	Mn	manganese 54.94	43	ည	te	75	Re	rhenium	107		1000		61	Pm	promethium	co	S 2	N neptunium
_								9	24	ပ်	chromium 52.00	42	Ø	molybdenum	74	>	tungsten	106	Sg	seaborgium		09	ž	neodymium 144.2	co	76	uranium 238.0
		nber	- -		weight			2	23	>	vanadium 50.94	41	q	miobium	73	F	tantalum	105	Db	dubnium		59	ሗ	praseodymium 140.9	50	- C	protactinium 231.0
	Key:	atomic number	Svmbo	name	standard atomic weight			4	22	F	titanium 47.87	40	Zr	zirconium	72	Ŧ	hafnium 178 5	104	峜	rutherfordium		58	ပီ	cerium 140.1	6) F	thorium 232.0
	1				_			ю	21	လွင	scandium 44.96	39	>	yttrium	57-71	lanthanoids		89-103	actinoids		<u> </u>	25	La	lanthanum 138.9	Co	0 <	Ac actinium
	2	4	Be	beryllium	9.012	12	Ma	magnesium 24.31	20	Ca	calcium 40.08	38	Š	strontium	2010	Ba	barium 137.3	88	Ra	radium			_				1
- I	hydrogen [1.007; 1.009]	3	=	lithium	[6.938; 6.997]	1	Na	sodium 22.99	19	¥	potassium 39.10	37	Rb	rubidium	55	Cs	caesium	87	Ŧ	francium			1				



Notes

doi:10.1351/PACREP-1009-14). The uncertainty in the last digit of the standard atomic weight value is listed in parentheses following the value. In the absence of parentheses, the uncertainty is one in that last digit. An interval in square brackets provides the lower and upper bounds of the standard atomic weight for that element. No values are listed for elements with no stable isotopes. See PAC for more details. - IUPAC 2009 Standard atomic weights abridged to four significant digits (Table 4 published in Pure Appl. Chem. 83, 359-396 (2011);

For updates to this table, see iupac.org/reports/periodic_table/. This version is dated 21 January 2011. Copyright © 2011 IUPAC, the International Union of Pure and Applied Chemistry.



[&]quot;Aluminum" and "cesium" are commonly used alternative spellings for "aluminium" and "caesium."

Increasing electronegativity

8A				Kr 3.0	Xe 2.6		
	7A	F	CI 3.0	Br 2.8	I 2.5	At 2.2	
	6A	3.5	S 2.5	Se 2.4	Te 2.1	Po 2.0	
	5A	N 3.0	P 2.1	As 2.0	Sb 1.9	Bi 1.9	
	4A	C 2.5	Si 1.8	Ge 1.8	Sn 1.8	Pb 1.9	
	3A	B 2.0	Al 1.5	Ga 1.6	In 1.7	TI 1.8	
			2B	Zn 1.6	Cd 1.7	Hg 1.9	
			118	Cu 1.9	Ag 1.9	Au 2.4	
			Г	Ni 1.9	Pd 2.2	Pt 2.2	
			-8B-	Co 1.9	Rh 2.2	Ir 2.2	
			L	Fe 1.8	Ru 2.2	Os 2.2	
			7B	Mn 1.5	Тс 1.9	Re 1.9	
			6B	Cr 1.6	Mo 1.8	W 1.7	
			5B	V 1.6	Nb 1.6	Ta 1.5	
			4B	Ti 1.5	Zr 1.4	Hf 1.3	
			3B	Sc 1.3	Y 1.2	La-Lu 1.0-1.2	
_	2A	Be 1.5	Mg 1.2	Ca 1.0	Sr 1.0	Ba 0.9	Ra 0.9
$\frac{1}{4}$	H 2.1	Li 1.0	Na 0.9	K 0.8	Rb 0.8	Cs 0.7	F r 0.7

Electronegativities of the elements

Increasing electronegativity

Навчальне видання

Ельцов Сергій Віталійович Водолазька Наталія Олександрівна Ворошилова Юлія Володимірівна Василець Григорій Юрійович Корсун Олександр Миколайович Кравченко Олексій Андрійович

Медична хімія: Теорія та лабораторні роботи до першого модуля

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