## MINISTRY OF HEALTH REPUBLIC OF BELARUS GOMEL STATE MEDICAL UNIVERSITY

Department of general and bioorganic chemistry

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# **CHEMISTRY OF THE ELEMENTS**

Laboratory manual

Gomel 2006

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Пособие посвящено химии биогенных элементов. Рассмотрены вопросы строения, свойств и биогенных функций химических элементов s, p, и d -блоков. Предложенные задачи и упражнения призваны помочь лучше усвоить данную тему, исключительно важную для будущих врачей.

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#### CHAPTER 1 COMPLEX (COORDINATION) COMPOUNDS

#### **1.1. MAIN DEFINITIONS**

After reading this chapter, you should be able to:

> Define complex compounds, complexing agents and ligands;

> Describe classification of complex compounds according to nature of their ligands;

Discuss naming of complex compounds;

> Describe bonding in coordination complexes using VB Method and Crystal-field Theory; define magnetic properties of complex ions;

> Discuss metal-ligands equilibrium in water solutions and stability of complex compounds.

Complex (coordination) compounds are the compounds in which a number of covalent bonds formed by a central atom exceed its ordinary covalence number.

For example:  $FeCl_3$  is a simple compound,  $[FeCl_6]^{3-}$  is a complex compound.

Our understanding of the nature of complex compounds is the result of the classic work of **Alfred Werner**. According to his theory, complex compounds consist of:

A central atom (ion), known as a complexing agent;

Ligands (ions or polar molecules);

 $\blacktriangleright$  Ions of outer sphere (counter ions).

Central atoms are usually metals, seldom nonmetals (B, P, and Si). They are characterized by their:

#### (a) oxidation numbers;

#### (b) coordination numbers.

A coordination number is a number of covalent bonds, which a central atom forms with its ligands. Given below are the most typical coordination numbers corresponding to definite charges of the central ion:

| Coordination number |
|---------------------|
| 2                   |
| 4, 6                |
| 4, 6                |
| 6, 8                |
|                     |

**Ligands** are ions or polar molecules that surround the metals in complex ions. They contain one or several donor atoms bond directly to the metal ions. Depending on the number donor atoms they may be classified as:

#### ≻Monodentane:

(a) ions of monoprotic acids:

| $CN^{-}$ — cyano;               |
|---------------------------------|
| CNS <sup>-</sup> — thiocyanato; |
| $NO_2^-$ — nitro;               |
|                                 |
| H <sup>-</sup> — hydrido;       |
|                                 |
| $NH_3$ — ammine;                |
| NO — nitrosyl                   |
|                                 |
|                                 |

(a) anions of diprotic acids:

 $SO_4^{2-}$ — sulphato;  $CO_3^{2-}$ — carbonato;  $SO_3^{2-}$ — sulphito  $C_2O_4^{2-}$ — oxalate;

(b) molecules:

 $NH_2 - CH_2-CH_2-NH_2$  — ethylendiamine;  $NH_2-CH_2-COOH$  — glycine;

#### > Polydentane

Ethylenediaminetetraacetate ion (EDTA)

 $\begin{array}{c} \hline OOC - CH_2 \\ \hline OOC - CH_2 \end{array} \xrightarrow{N - CH_2 - CH_2 - N} \begin{array}{c} \hline CH_2 - COO^- \\ \hline CH_2 - COO^- \end{array}$ 

#### **CLASSIFICATION OF COMPLEX COMPOUNDS**

According to the nature of ligands complex compounds may be classified in a following way:

| > Aquacomplexes —                   | $[Cu(H_2O)_4]SO_4;$                                       |
|-------------------------------------|---|
| ➤ Ammines —                         | $[Ni(NH_3)_4]Cl_2;$                                       |
| Hydrocomplexes —                    | $K_2[Zn(OH)_4];$  |
| Acidocomplexes —                    | $K_4[Fe(CN)_6];$  |
| ➤ Carbonyles —                      | $[Fe(CO)_5];$   |
| Complex compounds of a mixed type — | Na[Al(OH) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ]; |

> Chelate complex compounds (from the Greek *chele* — claw) — complex compounds containing bi- or polydentane ligands forming cycles.

$$\begin{array}{c} CH_2 - NH_2 \\ | \\ CH_2 - NH_2 \end{array} Cu \begin{array}{k} & NH_2 - CH_2 \\ | \\ NH_2 - CH_2 \end{array}$$

Chelate compounds also include intracomplex compounds in which the central atom is a part of a ring and forms covalent bonds in various ways.



The intracomplex compounds include very important natural complexes — hemoglobin and chlorophyll.

#### **1.2. NAMING OF COORDINATION COMPOUNDS**

The rules for naming complex (coordination) compounds are as follows:

 $\blacktriangleright$  The cation is named before the anion, as in the case for other ionic compounds;

 $\succ$  Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last;

> The names of ionic ligands end with the letter o, whereas a neutral ligand is usually called by the name of the molecule. The exceptions are  $H_2O$  (aqua), CO (carbonyl), NH<sub>3</sub> (ammine);

 $\succ$  When several ligands of a particular kind are present, we use the Greek prefixes di-, tri-, tetra-, penta-, and hexa- to name them. If the ligand itself contain a Greek prefix, we use the prefixes bis-, tris-, and tetrakis to indicate the number of ligands present;

 $\succ$  The oxidation number of the metal is written in Roman numerals following the name of the metal;

> If the complex is an anion, its name ends in ate (table 1).

#### Table 1

| In cationic complexes | In anionic complexes |
|-----------------------|----------------------|
| Aluminum              | Aluminate            |
| Chromium              | Chromate             |
| Cobalt                | Cobaltate            |
| Copper                | Cuprate              |
| Gold                  | Aurate               |
| Iron                  | Ferrate              |
| Silver                | Argentate            |
| Tin                   | Stannate             |
| Lead                  | Plumbate             |
| Tungsten              | Tungstate            |
| Nickel                | Nickelate            |
| Mercury               | Mercurate            |

#### Name of metals

#### **EXAMPLE 1**

Give an oxidation and coordination numbers of a central atoms in the following complex compounds: (a)  $K_2[Fe(CN)_5NH_3]$ , (b)  $[Co(H_2O)_4Cl_2]Cl$ , (c)  $[Ni(CO)_4]$ . Give the systematic name for them.

#### ANSWER

(a) The complex ion is an anion and it bears two negative charges. It contains two types of ligands: the anion  $CN^-$  and the  $NH_3$  molecules. An oxidation number of the iron atom may be calculated in a following way:  $\mathbf{x} - 5 = -2$ , where x is an oxidation number of the iron atom. Thus  $\mathbf{x} = +3$ . A coordination number of the iron atom is six since it forms six covalent bonds with six monodentane ligands. The compound is called potassium pentacyanoammineferrate (III).

(b) The complex ion is a cation and it bears one positive charge. It contains two types of ligands: two chloride anion and four water molecule. An oxidation number of the cobalt atom may be calculated in a following way:  $\mathbf{x} - 2 = +1$ , where  $\mathbf{x}$  is an oxidation number of the cobalt atom. Thus  $\mathbf{x} = +3$ . A coordination number of the cobalt atom is six since it forms six covalent bonds with six monodentane ligands. The compound is called dichlorotetraaquacobalt (III) chloride.

(c) The CO ligands are neutral species and the nickel atom bears no net charge, so the compound is called tetracarbonylnickel (0), or, more commonly nickel tetracarbonyl. A coordination number of the nickel atom is four since it forms four covalent bonds with four monodentane ligands.

#### **1.3. BONDING IN COORDINATION COMPOUNDS**

The formation of complex compounds may come about either through a donoracceptor or through an electrostatic interaction, in general through both of them simultaneously. At present the Valence Bond (VB) Method and the Crystal Field theory are widely employed to explain both the formation of complexes and their properties.

According to VB Method, complexes are formed through a donor-acceptor interaction mainly of the unpaired electron pairs of Ligands and the vacant orbitals of the metal. The configurations of complex ions depend upon a type of hybridization of complexing agents and their coordination numbers (CN).



Fig.1. Common configurations of complex ions

**Crystal-field theory** is based on the assumption that purely electrostatic interaction operate between a metal and ligands. It takes into account the effect of ligands on the state of the electrons in metals.

Studies of many coordination complexes revealed a common pattern in field strength of various ligands. This pattern is described by the **spectrochemical series**, in which ligands are listed in the order of increasing strength of their fields:

#### $I^- > Br^- > CI^- > F^- > OH^- > H_2O > NH_3 > en > NO_2^- > CN^- > CO$

In an atom or ion, free or placed in a spherical symmetry field, all five d-orbitals of a sub-shell will have the same energy, or may be said to be **degenerate.** When an atom (ion) has an octahedral, tetrahedral, or other field (less symmetrical than spherical), the energy of the d-orbitals is altered and the d sub-shell is split. **The crystal-field splitting** ( $\Delta$ ) depends upon the metals and ligands. When ligands' field is weak  $\Delta$  is not large and the electrons will fill the five d orbitals in succession (according to Hund's rule). When the ligand's field is strong the value of  $\Delta$  is large, and in that case d orbitals of lower energy are first filled with electrons, before orbitals of higher energy begin to be filled (against Hund's rule). The electrons distribution of Fe<sup>3+</sup> ion during formation of the octahedral complexes [FeF<sub>6</sub>]<sup>3-</sup> and [Fe(CN)<sub>6</sub>]<sup>3-</sup> is represented in fig. 2.

Because F– is a weak-field ligand with a small value of  $\Delta$ , Hund's rule prevails, and  $[\text{FeF}_6]^{3-}$  is a high-spin complex. The opposite holds true for the strong-field ligand CN<sup>--</sup>. In  $[\text{Fe}(\text{CN})_6]^{3-}$  the electrons the electrons are preferentially paired in the lower orbitals, and low-spin complex results. In general, we can reliably predict the magnetic properties of a complex ion from the electron configuration and the nature of the ligands.



**Fig.2.** Energy-level diagrams for  $[FeF_6]^{3-}$  and  $[Fe(CN)_6]^{3-}$ 

#### **1.4. STABILITY OF COMPLEX COMPOUNDS**

Dissociation of complex compounds occurs in two steps:

> Primary dissociation, which proceeds like ionization of strong electrolytes

$$K_3 [Fe (CN)_6] \rightarrow 3 K^+ + [Fe (CN)_6]^{3-1}$$

Secondary dissociation, which proceeds like ionization of weak electrolytes

$$[Fe (CN)_6]^{3-} \leftrightarrow Fe^{3+} + 6 CN^{-}$$

Metal-ligands equilibrium is characterized by an equilibrium constant called the formation (stability) constant  $K_{f}$ :

$$\mathbf{K}_{\mathrm{f}} = \frac{\left[Fe\left(CN\right)_{6}\right]^{3-}}{\left[Fe^{3+}\right] \times \left[CN^{-}\right]^{6}}$$

The formation constant is a measure of the stability of a complex: the higher  $K_f$ , the more is complexes' stability.  $K_f$  indicates only complex ion stability or instability; but the reason for its stability lies in a complex compound structure.

> The smaller are metals' radii and large are their charges the higher is stability of complex ions.

 $\succ$  Polydentane ligands form more stable complex compounds in comparison with monodentane ligands. Especially stable are the chelates. This phenomenon is known as the *chelate effect*.

#### **EXAMPLE 2**

Write equations for primary and secondary dissociation of  $K_2[HgI_4]$ . Give the expression for its formation constant.

#### **ANSWER**

(a) primary dissociation:  $K_2[HgI_4] \rightarrow 2 K^+ + [HgI_4]^-$ 

(b) secondary dissociation:  $[HgI_4]^{2-} \leftrightarrow Hg^{2+} + 4^{-}I$ 

$$\mathbf{K}_{\mathrm{f}} = \frac{\left[HgI\right]^{2-}}{\left[Hg^{2+}\right] \times \left[I^{-}\right]^{4}}$$

#### **1.5. LABORATORY WORK «COMPLEX COMPOUNDS»**

#### **Preparing of cationic complexes**

#### **TEST 1.** *Preparing of Cu (II) complex ammine.*

Prepare a precipitate of copper (II) hydroxide, and dissolve it in 1–2 mL of 25% ammonia solution. Mark a color of an obtained solution. Give a systematic name to the obtained complex compound. Write the equations of fulfilled reactions.

 $CuSO_4 + 2 NaOH \rightarrow Cu (OH)_2 \downarrow + Na_2SO_4$  $Cu (OH)_2 + 4 NH_3 \leftrightarrow [Cu(NH_3)_4](OH)_2$ 

#### **TEST 2.** Preparing of Ni (II) complex ammine.

Prepare a precipitate of nickel (II) hydroxide, and dissolve it in 1–2 mL of 25% ammonia solution. Mark a color of an obtained solution. Give a systematic name to the obtained complex compound. Write the equations of fulfilled reactions.

 $NiSO_4 + 2 NaOH \rightarrow Ni (OH)_2 \downarrow + Na_2SO_4$  $Ni(OH)_2 + 4 NH_3 \leftrightarrow [Ni (NH_3)_4](OH)_2$ 

#### **Preparing of anionic complexes**

#### TEST 3. Preparing of Bi (III) acidocomplex.

Pour 3–4 drops bismuth (III) nitrate solution to a test-tube and add some drops of potassium iodide up to the formation of dark bismuth (III) iodide precipitate. Dissolve the obtained precipitate in 1-2 mL of potassium iodide solution. What is the color of an obtained solution? Give a systematic name to the obtained complex compound. Write the equations of fulfilled reactions.

Bi  $(NO_3)_3 + 3 \text{ KI} \rightarrow \text{BiI}_3 \downarrow + 3 \text{ KNO}_3$ 

 $BiI_3 + KI \leftrightarrow K [BiI_4]$ 

#### **TEST 4.** Preparing of Hg (II) acidocomplex.

Pour 3-4 drops mercury (II) nitrate solution to a test-tube and add some drops of potassium iodide up to the formation of red mercury (II) iodide precipitate. Dissolve the obtained precipitate in 1-2 mL of potassium iodide solution. What is the color of an obtained solution? Give a systematic name for the obtained complex compound. Write the equations of fulfilled reactions.

 $Hg (NO_3)_2 + 2 KI \rightarrow HgI_2 \downarrow + KNO_3$  $HgI_2 + 2 KI \leftrightarrow K_2 [HgI_4]$ 

#### **TEST 5.** Preparing of hydroxocomplexes.

Pour 3–4 drops of zinc, chromium and aluminum salts solutions to each of the three test-tubes and add some drops of sodium hydroxide solution in to them up to the formation of hydroxides' precipitates. Mark color of obtained precipitates and dissolve them in the excess of alkali solution. Mark color of obtained solutions and give systematic names for the prepared complex compounds. Write the equations of fulfilled reactions.

 $ZnCl_{2} + 2 NaOH \rightarrow Zn (OH)_{2} \downarrow + 2 NaCl$   $Zn (OH)_{2} + 2 NaOH \leftrightarrow Na_{2} [Zn (OH)_{4}]$   $CrCl_{3} + 3 NaOH \rightarrow Cr (OH)_{3} \downarrow + 3 NaCl$   $Cr (OH)_{3} + 3 NaOH \leftrightarrow Na_{3} [Cr(OH)_{6}]$   $Al (NO_{3})_{3} + 3 NaOH \rightarrow Al (OH)_{3} \downarrow + 3 NaNO_{3}$  $Al (OH)_{3} + NaOH \leftrightarrow Na[Al(OH)_{4}]$ 

#### **TEST 6.** Intracomplex compounds

Pour 3 drops of iron (III) chloride solution into each of the three test tubes. Add 3 drops of NaOH solution into two of them. Mark the color of the obtained precipi-

tate. Dissolve a precipitate in the first test tube in the excess of 2 N oxalic acid solution. Mark the color of a prepared solution. Dissolve a precipitate in the second test tube in the excess of 2 N citric acid solution. Mark the color of a prepared solution.

Add 1–2 drops of 0,01 N NH<sub>4</sub>CNS solution into each of the test tube, including a test tube filled by initial FeCl<sub>3</sub> solution. Mark color of all prepared solutions. Does red-blood color appear in all the test tubes? Write the equations of fulfilled reactions.

Make a conclusion about stability of intracomplex compounds.

#### **Stability of complex compounds**

**TEST 7.** Silver complex compounds stability

Prepare a precipitate of silver (I) chloride and dissolve it in 1–2 mL of 25% ammonia solution. Mark a color of an obtained solution. Give a systematic name to the obtained complex compound. Add some drops of potassium iodide solution into it. Mark a color of an obtained precipitate. Compare Ksp of AgI and Kf of  $[Ag(NH_3)_2]^+$ . Make a conclusion about stability of silver compounds. Write the equations for fulfilled reactions.

 $2 \text{ AgNO}_3 + 2 \text{ NaOH} \rightarrow \text{Ag}_2\text{O} \downarrow + 2 \text{ NaNO}_3 + \text{H}_2\text{O}$ Ag\_2O + 4 NH<sub>4</sub>OH  $\rightarrow 2 [\text{Ag} (\text{NH}_3)_2] \text{ OH} + 3 \text{ H}_2\text{O}$ [Ag (NH<sub>3</sub>)<sub>2</sub>]OH + KI  $\rightarrow \text{AgI} \downarrow + 2 \text{ KOH} + 2 \text{ NH}_3 \uparrow$ 

#### **TEST 8.** Stability of thiocyanate complex compounds in water and alcohols

Pour 3–4 drops of cobalt (II) nitrate solution to a test-tube and add 8–10 drops of ammonium thiocyanate saturated solution. Mark a color of a prepared solution and give a systematic name for an obtained complex compound. Divide a solution into two test tubes. Add 3–5 drops of amyl alcohol into the first and 10 drops of water into the second test tubes. Mark changes in color in both test tubes. Make a conclusion about stability of complex compounds in water and alcohol media. Write the equations of fulfilled reactions.

 $Co (NO_3)_2 + 4 NH_4CNS \leftrightarrow (NH_4)_2 [Co(CNS)_4] + 2 NH_4Cl$ 

**TEST 9.** Aluminum complex compounds stability.

Prepare a solution of sodium tetrahydroxoaluminate (III) (experiment N 5) and add 5–6 drops of NH<sub>4</sub>Cl saturated solution. Mark a color of an obtained precipitate.

Make a conclusion about stability of aluminums complex compounds. Write the equations of fulfilled reactions.

 $\begin{array}{l} Al(NO_3)_3 + 4 \text{ NaOH} \leftrightarrow Na[Al(OH)_4] + 3 \text{ NaNO}_3\\ Na[Al(OH)_4] + 3 \text{ NH}_4Cl \rightarrow Al(OH)_3 \downarrow + 3 \text{ NaCl} + 3 \text{ NH}_4OH \end{array}$ 

#### **1.6. MATERIALS FOR SELF-CONTROL**

**1.** Calculate charges of the following complex ions. Add ions of outer sphere. Give systematic names for the complex compounds:

**2.** Calculate charges of central ions in complex compounds. Give systematic names for the following complex compounds:

 $\begin{array}{cccc} x & x & x & x \\ K_2[PtBr_4]; Na_4[Fe(CN)_6]; [Pb(NH_3)_6]Cl_4; [Cu(H_2O)_4]SO_4; \end{array}$ 

x x [Cr(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub>; K[Co(H<sub>2</sub>O)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>].

**3.** Give a definition for the formation constant. Write an equation for  $[Fe(CN)_6]^{4-1}$  ionization and mathematical equation for its K f.

**4.** Write formulas of the following complex compounds:

(a) Pentaamminechloroplatinum (IV) chloride

(b) Potassium tetrahydroxochromate (III)

(c) Hexaammincobalt (III) bromide

#### CHAPTER 2

#### **S-BLOCK – ELEMENTS**

After reading this chapter, you should be able to:

> Derive the <u>electron configurations</u> of the s-block elements and their simple ions;

> Recall the characteristic properties of the s-block elements essential to life:

(a) Their acting in Redox reactions.

(b) Their ability to form a range of complex compounds with different ligands;

(c) Their salts hydrolysis;

(d) Basic character of their oxides and hydroxides, amphoteric character of BeO and Be(OH).

> Remember the equations of test reactions on cations of s-block elements.

#### 2.1. GENERAL PROPERTIS OF S-BLOCK ELEMENTS

s-Block elements — are chemical elements with electron configuration  $ns^x$ , where x is a number of electrons (1–2), n is a principal quantum number.

They are members of main group's elements. Most of them are metals, known as Alkali and Alkaline Earth, but H and He are nonmetals.

Table 2

| Sym-<br>bol | Content<br>in earth's crust,<br>% by mass | Electron configuration nS <sup>1</sup>   | R,<br>nm | I,<br>mV | φ°,<br>V |
|-------------|---|--|----------|----------|----------|
| Li          | 6.5×10 <sup>-3</sup>                      | $1s^{2}2s^{1}$   | 0.155    | 5.39     | -3.05    |
| Na          | 2.5                                       | $1s^{2}2s^{2}2p^{6}3s^{1}$   | 0.189    | 5.14     | -2.71    |
| K           | 2.6                                       | $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{1}$   | 0.236    | 4.34     | -2.93    |
| Rb          | 1.5×10 <sup>-2</sup>                      | $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{1}$                      | 0.248    | 4.176    | -2.93    |
| Cs          | 3.7×10 <sup>-4</sup>                      | $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6\boldsymbol{6s^1}$          | 0.268    | 3.89     | -2.92    |
| Fr          |   | $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^1$ | 0.280    | 3.98     |          |

## The Alkali Metals

(The Group IA elements)

The Alkali Metals are the most electropositive (or the least electronegative) elements known. In other words they are the most active metals:  $Me - e^- \rightarrow Me^+$ .

They exhibit many similar properties because of their analogues electrons configurations. From top to bottom their orbital radii (R) increase, electronegativity ( $\chi$ ) and ionization potential (I) decrease. Thus the metallic character increases in the same direction.

From their electron configuration we expect the oxidation number of these elements in their compounds to be +1, except H.

Their main compounds are:

> Oxides Me<sub>2</sub>O
> Hydroxides MeOH, which are basic by nature: Na<sub>2</sub>O + H<sub>2</sub>O → 2 NaOH Na<sub>2</sub>O + 2 HCl → 2 NaCl + H<sub>2</sub>O NaOH → Na<sup>+</sup> + OH<sup>-</sup>
2 NaOH + H<sub>2</sub>SO<sub>4</sub> → Na<sub>2</sub>SO<sub>4</sub> + 2 H<sub>2</sub>O Their basicity increases from top to bottom.
> Hydrides (MeH) are crystal solids easily decomposed by water and acids: NaH + H<sub>2</sub>O → NaOH + H<sub>2</sub>

 $NaH + HCl \rightarrow NaCl + H_2$ 

Na and K are most abundant in nature but because of their activity they never occur naturally in elemental form; they are found combined with halide, sulfate, carbonate and silicate ions.

Na and K are essential elements of living matter. Their content is a human body is more than  $1 \times 10^{-2}$ % by mass thus they are *macro elements*.

Li and Cs with content  $1 \times 10^{-5}$ % by mass are *microelements*.

This classification of chemical elements was developed by V. Vernadsky (the founder of the biosphere theory). He also proved that those elements are consumed by living organism, which form soluble compounds with the main ions of hydrosphere ( $OH^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $CI^-$ ) or gases (vapors) of atmosphere.

The Alkaline Earth Metals (Group IIA) are somewhat less electronegative and less reactive than the alkali metals. Except for the first member of the family, beryllium, which resembles aluminum in some respects, the alkaline earth metals have similar chemical properties. They are:

 $\succ$  soft, but harder than alkali metals;

> reactive, but not as reactive as alkali metals;

➤ ionization energies are not as low as alkali metals;

 $\succ$  salts less soluble than those of the alkali metals;

 $\succ$  higher cation charge concentrated on smaller cations makes it hard to pull apart ionic lattices.

#### Table 3

| Sym-<br>bol | Content<br>in earth's<br>crust, %<br>by mass | Electron configuration ns <sup>1</sup>   | R, nm | I,<br>mV | φ°,<br>V |
|-------------|--|--|-------|----------|----------|
| Be          | 6×10 <sup>-4</sup>                           | $1s^22s^1$   | 0.112 | 9.32     | -1.84    |
| Mg          | 2.1  | $1s^22s^22p^63s^1$   | 0.160 | 7.64     | -2.36    |
| Ca          | 3.6  | $1s^22s^22p^63s^23p^64s^1$   | 0.197 | 6.11     | -2.86    |
| Sr          | 4×10 <sup>-2</sup>                           | $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1$                                      | 0.215 | 5.69     | -2.88    |
| Ba          | $5 \times 10^{-2}$                           | $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^6\mathbf{6s^1}$              | 0.222 | 5.21     | -2.91    |
| Ra          | $1 \times 10^{-10}$                          | $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^1$ | 0.280 | 5.27     | -2.91    |

#### The Alkaline Earth Metals

(The Group IIA elements)

The oxidation number of alkaline earth metals in the combined form is always +2. Their main compounds are:

- > Oxides **MeO**;
- ➢ Hydroxides Me (OH)₂;
- ➢ Hydrides MeH₂

Oxides and hydroxides are basic by nature, except BeO and Be (OH) <sub>2</sub> which exhibit amphoteric (amphiprotic) properties. From top to bottom with the increase in elements' metallic properties there is an increase in basicity of their oxides and hydroxides.

Ca and Mg are essential elements of living matter. Their content is a human body is more than  $1 \times 10^{-2}$ % by mass thus they are *macro elements*.

| Table 4<br>Biologic | al functions               | of s-block elements  |  |  |
|---------------------|----------------------------|--|--|--|
| Element             | Content in a<br>human body | Topography<br>in a human body  | <b>Biological fuctions</b>   | Medicines (drugs)  |
| $\mathrm{Na}^+$     | 100g/70kg<br>or 0.14%      | Present in all tissues, in-<br>tracellular and intracellu-<br>lar fluids | <ul> <li>Hold water in body tissues</li> <li>Adjust acid-base balance</li> <li>Involved in nerve impulse transmission</li> <li>Maintains osmotic pressure</li> <li>Excessive in take of Na<sup>+</sup> may cause a hypertension. Recommended intake 2.4–3.000 mg /day</li> </ul>   | NaCl – plasma substitution,<br>0.9% - isotonic solutions, $10%$ –<br>to cure purulent wounds<br>NaHCO <sub>3</sub> (sodium bicarbonate) –<br>mtacidic drug<br>HCO <sub>3</sub> <sup>-+</sup> H <sup>+</sup> $\rightarrow$ CO <sub>2</sub> + H <sub>2</sub> O<br>Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ×10H <sub>2</sub> O(borax) – for<br>hisinfection<br>NaNO <sub>2</sub> – heart diseases |
| $\mathbf{K}^+$      | 140g/70 kg<br>or 0.2%      | Present in all tissues, intra-<br>cellular and intracellular<br>fluids   | <ul> <li>Act at cell membranes in transmitting electrochemical impulses in nerve and muscle fibers.</li> <li>Act in balancing the activity of food intake and waste removal from cells.</li> <li>It is necessary for protein synthesis.</li> <li>It is necessary for protein synthesis.</li> <li>Huid balance</li> <li>Muscle contraction</li> <li>Prevent <sup>137</sup>Cs accumulation</li> <li>K<sup>+</sup> deficiency causes weakness, mental confusion, and possible death. Excessive intake causes weakness and possible vomiting. Estimated minimum requirements are 2000 mg/day.</li> </ul> | KCI — to maintain electrolyte<br>valance<br>KI — to protect against iodine<br>deficiency, to treat endemic goiter<br>myxedema.   |

| Element          | Content in a<br>human body | Topography<br>in a human body  | <b>Biological fuctions</b>   | Medicines (drugs)   |
|------------------|----------------------------|--|--|---|
| Mg <sup>+2</sup> | 19g/70kg<br>or 0.027%      |  | <ul> <li>Bone mineralization</li> <li>Protein synthesis</li> <li>Enzymatic reaction</li> <li>Nerve transitions</li> <li>Nerve transitions</li> <li>Symptoms of deficiency are weakness, confusion, hypertension, arrhythmia, depressed pancreatic hormone secretion, growth failure, behavioral disturbance, and muscle spasms. Recommended intakes for adults 280–350 mg/day.</li> </ul>  | MgO (burnt magnesia) — antacid<br>MgO + 2 HCl $\rightarrow$ MgCl <sub>2</sub> + H <sub>2</sub> O<br>MgSO <sub>4</sub> (white magnesia) — 20%<br>solution as hypertonic solution<br>at hypertension.       |
| Ca <sup>+2</sup> | 1000g/70kg<br>or 1.4%      | 99% of Ca is concen-rated<br>in bones as<br>Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F(in teeth)<br>Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F(in teeth)<br>1% of Ca is in blood plasma,<br>muscles, liver, kidneys and<br>other organs in the ionized<br>and complexed forms. | <ul> <li>The principal skeletal mineral in bones and teeth.</li> <li>Blood clotting</li> <li>Nuscle contraction</li> <li>Nerve transmission</li> <li>Nerve transmission</li> <li>Heart action</li> <li>Heart action</li> <li>Protection of a human body from <sup>90</sup>Sr accumulation. Ca deficiency can result in a range of health problems: osteoporosis, stunted childhood growth, possible hypertension, and preeclampsia and colon cancer. The adults' person should receive from 800 up to 1100 mg/day with foodstuff and water.</li> </ul> | <b>CaSO<sub>4</sub>×2H<sub>2</sub>O</b> — gypsum<br>CaCl <sub>2</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , CaC <sub>2</sub> O <sub>4</sub> and<br>other salts combined with vit <b>D</b> . |

#### 2.2. LABORATORY WORK «QUALITATIVE REACTIONS ON THE CATIONS OF S-BLOCK METALS»

**TEST Nº 1** *Qualitative reactions on*  $K^+$ 

**1.** Sodium hexanitrocobaltate (III)  $Na_3$  [Co(NO<sub>2</sub>)<sub>6</sub>] interacts with potassium cations with the formation of yellow crystals of potassium-sodium hexanitrocobaltate (III) according to the reaction:

 $2 \text{ KCl} + \text{Na}_3 \left[\text{Co}(\text{NO}_2)_6\right] \rightarrow \text{K}_2\text{Na} \left[\text{Co}(\text{NO}_2)_6\right] \downarrow + 2 \text{ NaCl}$ 

 $2K^{+} + Na^{+} + [Co(NO_2)_6]^{3-} \rightarrow K_2Na [Co (NO_2)_6] \downarrow$ 

The reaction must be fulfilled in a neutral or weak acidic media because a reagent undergoes decomposition in basic or strong acidic media:

 $[Co(NO_2)_6]^{3-} + 3 \text{ OH}^- \rightarrow Co(OH)_3 \downarrow + 6 \text{ NO}_2^ [Co(NO_2)_6]^{3-} + 10 \text{ H}^+ \rightarrow 2 \text{ Co}^{2+} + 5 \text{ NO} + 7\text{NO}_2 + 5 \text{ H}_2\text{O}$ 

Pour 2–3 drops of any potassium salt solution into a test tube; add one drop of a dilute acetic acid solution and 2 drops of sodium hexanitrocobaltate (III) solution. What can you see?

**2.** Tartaric acid  $H_2C_4H_4O_6$  and its sodium salt  $NaHC_4H_4O_6$  interact with potassium cations with the formation of white crystals the potassium hydrotartrate:

 $\mathrm{KCl} + \mathrm{NaHC_4H_4O_6} \rightarrow \mathrm{KHC_4H_4O_6} \downarrow + \mathrm{NaCl}$ 

 $K^+ + HC_4H_4O_6^- \rightarrow KHC_4H_4O_6\downarrow$ 

When tartaric acid is used as a reagent it is necessary to add sodium acetate in order to neutralize a forming hydrochloric acid which may cause dissolving of an insoluble salt precipitate:

 $\mathrm{KCl} + \mathrm{H_2C_4H_4O_6} + \mathrm{CH_3COONa} \rightarrow \mathrm{KHC_4H_4O_6} \downarrow + \mathrm{NaCl} + \mathrm{CH_3COOH}$ 

 $K^+$  determination must be carried out in neutral or weak acidic media since a precipitate is readily dissolved in strong acids and bases solutions:

 $\mathrm{KHC_4H_4O_6}\downarrow + \mathrm{HCl} \rightarrow \mathrm{H_2C_4H_4O_6} + \mathrm{KCl}$ 

 $\mathrm{KHC_4H_4O_6} \downarrow + \mathrm{KOH} \rightarrow \mathrm{K_2C_4H_4O_6} + \mathrm{H_2O}$ 

More over, it is better to fulfill an experiment at low temperature because heating may cause a precipitate dissolving.

Pour 2–3 drops of any potassium salt solution into a test tube; add one drop of a sodium acetate solution and 2 drops of tartaric acid solution. In order to accelerate crystallization process rubs a test tube with a glass stick. What can you see?

**TEST № 2.** Qualitative reactions on Na<sup>+</sup>

**1.** Potassium hexahydroxostibiate (Y) калия K [Sb (OH)  $_6$ ] interacts with sodium cations with the formation of white crystals of sodium hexahydroxostibiate (Y):

 $NaCl + K [Sb (OH)_6] \rightarrow Na [Sb (OH)_6] \downarrow + KCl$ 

 $Na^{+} + [Sb (OH)_{6}]^{-} \rightarrow Na [Sb (OH)_{6}] \downarrow$ 

Pour 2–3 drops of any sodium salt solution into a test tube and add 3 drops of potassium hexahydroxostibiate (Y) solution. What can you see?

**TEST Nº 3.** Qualitative reactions on  $Mg^{+2}$ 

**1.** Ammonium carbonate  $(NH_4)_2CO_3$  interacts with magnesium salts with the formation of a basic salt  $(MgOH)_2CO_3$  precipitate:

 $2 \operatorname{MgCl}_{2} + 2 (\operatorname{NH}_{4})_{2} \operatorname{CO}_{3} + \operatorname{H}_{2} \operatorname{O} \rightarrow (\operatorname{MgOH})_{2} \operatorname{CO}_{3} \downarrow + \operatorname{CO}_{2} \uparrow + 4 \operatorname{NH}_{4} \operatorname{Cl}$  $\operatorname{Mg}^{2^{+}} + 2 \operatorname{CO}_{3}^{2^{-}} + \operatorname{H}_{2} \operatorname{O} \rightarrow (\operatorname{MgOH})_{2} \operatorname{CO}_{3} \downarrow + \operatorname{CO}_{2} \uparrow$ 

Pour 2-3 drops of a magnesium salt solution and add some drops of ammonium

carbonate. What can you see?2. Strong bases and aqueous ammonia solution interact with magnesium salts with the formation of an insoluble magnesium hydroxide according to the following equation:

 $Mg^{2+} + 2 OH^{-} \rightarrow Mg (OH)_{2} \downarrow$ 

Mg (OH)<sub>2</sub> is readily dissolved in acids and ammonium salts:

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

Mg (OH)  $_2$  + 2 NH $_4^+ \rightarrow$  Mg $^{2+}$  + 2 NH $_4$ OH

Pour 2 drops of a magnesium salt solution into a test tube and add 2-3 drops of NaOH. What can you see? Try to dissolve the obtained precipitate in NH<sub>4</sub>Cl  $\mu$  HCl solutions.

**3.** Sodium hydro phosphate interacts with magnesium salts solutions with the insoluble phosphates formation. A reaction is readily going in basic solutions (pH = 9). To maintain such a medium an ammonium buffer solution is used (a mixture of NH<sub>4</sub>Cl  $\mu$  NH<sub>4</sub>OH solutions):

 $Mg^{2+} + HPO_4^{2-} + NH_4OH \rightarrow MgNH_4PO_4\downarrow + H_2O$ 

3 drops of an analyzed solution treat with 3 drops of  $NH_4Cl$  and 2 drops of  $NH_4OH$ . Add 3 drops of  $Na_2HPO_4$  solution and mix. What can you see?

**TEST №4**. Qualitative reactions on Ba<sup>+2</sup>

1. Ammonium carbonate  $(NH_4)_2CO_3$  interacts with barium salts with the formation of a BaCO<sub>3</sub> white precipitate:

BaCl<sub>2</sub> + (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> → BaCO<sub>3</sub> ↓ + 2 NH<sub>4</sub>Cl Ba<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup> → BaCO<sub>3</sub> ↓

The obtained precipitate is readily dissolved in strong and weak acids:

 $BaCO_3 + 2 H^+ \rightarrow Ba^{2+} + CO_2 \uparrow + H_2O$ 

Pour 3 drops of a barium salt solution and add 3 drops of  $(NH_4)_2CO_3$  solution. Try to dissolve a precipitate in hydrochloric and acetic acids. What can you see?

**2.** Sulfuric acid and its soluble salts interacts with barium salts solutions with the formation of white crystals of barium sulfate:

 $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2 \text{ HCl}$ 

 $\mathrm{Ba}^{2+} + \mathrm{SO_4}^{2-} \to \mathrm{BaSO_4} \downarrow$ 

BaSO<sub>4</sub> is insoluble in strong acids.

Pour 3 drops of BaCl<sub>2</sub> solution and 3 drops of a dilute H<sub>2</sub>SO<sub>4</sub>. Try to dissolve an obtained precipitate in hydrochloric acid. What can you see?

**3.** Potassium dichromate  $K_2Cr_2O_7$  interacts with barium salts solutions with the formation of yellow crystals of barium chromate:

 $2 \operatorname{Ba}^{2^+} + \operatorname{Cr_2O_7}^{2^-} + \operatorname{H_2O} \to 2 \operatorname{BaCrO_4} \downarrow + 2 \operatorname{H^+}$ 

A reaction is carried out with the addition of CH<sub>3</sub>COONa, which is used in order to neutralize hydrochloric acid and shift equilibrium to the right:

 $CH_3COO^- + H^+ \rightarrow CH_3COOH$ 

Pour 2 drops of  $BaCl_2$  solution and add 3 drops of  $CH_3COONa$  and 2 drops of  $K_2Cr_2O_7$  solution. What can you see?

**TEST Nº 5.** *Qualitative reactions on*  $Ca^{+2}$ 

**1.** Ammonium carbonate  $(NH_4)_2CO_3$  interacts with calcium salts' solutions with the formation of white crystals of calcium carbonate:

 $CaCl_{2} + (NH_{4})_{2}CO_{3} \rightarrow CaCO_{3} \downarrow + 2 NH_{4}Cl$ 

 $\operatorname{Ca}^{2+} + \operatorname{CO}_3^{2-} \rightarrow \operatorname{CaCO}_3 \downarrow$ 

The obtained precipitate is readily dissolved in strong and weak acids.

Pour 3 drops of  $CaCl_2$  solution and 3 drops of a  $(NH_{4)2}CO_3$  solution. Try to dissolve an obtained precipitate in hydrochloric and acetic acids. What can you see?

**2.** Ammonium oxalate  $(NH_4)_2C_2O_4$  interacts with calcium salts' solutions with the formation of white crystals of calcium oxalate:

$$\begin{aligned} & \operatorname{CaCl}_2 + (\operatorname{NH}_4)_2 \operatorname{C}_2 \operatorname{O}_4 \to \operatorname{CaC}_2 \operatorname{O}_4 \downarrow + 2 \operatorname{NH}_4 \operatorname{Cl} \\ & \operatorname{Ca}^{2^+} + \operatorname{C}_2 \operatorname{O}_4^{2^-} \to \operatorname{CaC}_2 \operatorname{O}_4 \downarrow \end{aligned}$$

Pour 2 drops of  $CaCl_2$  solution and add 2 drops of  $(NH_4)_2C_2O_4$  solution. Divide the obtained precipitate into two test tubes and try to dissolve it in hydrochloric and acetic acids. Make a conclusion.

**3.** Potassium hexacyanoferrate (II)  $K_4$  [Fe (CN) <sub>6</sub>] interacts with calcium salts' solutions with the formation of white crystals of Ca (NH<sub>4</sub>)<sub>2</sub>[Fe (CN) <sub>6</sub>]. A reaction is carried out in the presence of an ammonium buffer system (a mixture of NH<sub>4</sub>OH and NH<sub>4</sub>Cl):

$$CaCl_{2} + 2 \text{ NH}_{4}Cl + K_{4}[Fe(CN)_{6}] \rightarrow Ca(NH_{4})_{2}[Fe(CN)_{6}] \downarrow + 4 \text{ KCl}$$
$$Ca^{2+} + 2 \text{ NH}_{4}^{+} + [Fe(CN)_{6}]^{4-} \rightarrow Ca(NH_{4})_{2}[Fe(CN)_{6}] \downarrow$$

Pour 3 drops of  $CaCL_2$  solution in a test tube; add 3-4 drops of  $NH_4Cl$  and  $NH_4OH$  and 4-5 drops of potassium hexacyanoferrate (II) solutions. Heat a test tube in hot water. What can you see?

#### **TEST Nº6.** *Qualitative reactions on* $Sr^{+2}$

**1.** Ammonium carbonate  $(NH_4)_2CO_3$  interacts with strontium salts' solutions with the formation of white crystals of strontium carbonate:

 $\mathrm{Sr}^{2^+} + (\mathrm{NH}_4)_2\mathrm{CO}_3 \rightarrow \mathrm{Sr}\mathrm{CO}_3 \downarrow + 2 \mathrm{NH}_4^+$ 

The obtained precipitate is readily dissolved in strong and weak acids:

 $SrCO_3 + 2 \text{ H}^+ \rightarrow Sr^{2+} + CO_2 \uparrow + H_2O$ 

Pour 3 drops of  $SrCl_2$  solution and 3 drops of a  $(NH_4)_2CO_3$  solution. Try to dissolve an obtained precipitate in hydrochloric and acetic acids. What can you see?

**2.** Saturated solution of calcium sulfate CaSO<sub>4</sub><sup>-</sup>2H<sub>2</sub>O (gypsum water) interacts with strontium salts' solutions with the formation of white crystals of strontium sulfate:

 $\mathrm{Sr}^{2^+} + \mathrm{SO_4}^{2^-} \longrightarrow \mathrm{SrSO_4} \downarrow$ 

Heating may accelerate a reaction.

Pour 3 drops of  $SrCl_2$  solution into a test tube and add 3 drops of a  $CaSO_4 2H_2O$ . Heat a solution in boiling water. What can you see?

#### 2.3. EXCERCISES FOR THE SELF CONTROL

**1.** Write the electron configurations for atoms and cations the following for s-block elements:

(a) Na and  $Na^+$ 

(b)  $Ca^0$  and  $Ca^{2+}$ 

(c) Sr and  $Sr^{2+}$ 

(d)  $Fr and Fr^+$ 

**2.** Write the equations for the chemical reactions, which prove the amphoteric nature of  $Be(OH)_2$ .

**3.** Discuss biological properties of calcium in vivo. Write the equations for the chemical reactions which lie at the bottom of bone tissues formation.

4. Write the equations for the following salts hydrolysis:

(a)  $KF(b) Li_2CO_3$ 

(c)  $Mg(NO_3)_2$  (d)  $Na_3PO_4$ 

#### CHAPTER 3

#### **p-BLOCK ELEMENTS**

After reading this chapter, you should be able to:

 $\succ$  Derive the <u>electron configurations</u> of the p-block elements and their simple ions,

> Recall the characteristic properties of the p-block elements essential to life:

(a) Their acting in Redox reactions.

(b) Their ability of p-block metals to form a range of complex compounds with different ligands;

(c) Their salts hydrolysis;

> Basic character of their oxides and hydroxides, amphoteric character of BeO and Be(OH)

> Remember the equations of test reactions on cations of p-block elements.

#### **3.1. GENERAL PROPERTIS OF P-BLOCK ELEMENTS**

p-Block Elements are characterized by  $ns^2np^x$  electron configurations, where *x* is a number of valence electrons (1–6).

p-Block Elements are subdivided into metals and non-metals. A diagonal **B-At** separates p-Block Elements into metals and non-metals.



In group from top to bottom there is an increase in metallic and decrease in nonmetallic properties of elements.

Their main compounds are:

> oxides 
$$\rightarrow$$
 amphoteric — Al<sub>2</sub>O<sub>3</sub>, SnO

 > Hydrogen compounds, which exhibit basic (NH<sub>3</sub>, PH<sub>3</sub>) and acidic properties (H<sub>2</sub>S, HCl).

The essential macro elements of p-block are: C, O, N, P, S, Cl (table 5).

Most p-elements are microelements, which also fulfill important biological functions in a human body (table 6).

#### The chemical properties of p-block elements

**1.** Most oxides and hydroxides of p-block metals (Al(OH)<sub>3</sub>, Sn(OH)<sub>2</sub>, Pb(OH)<sub>2</sub>, Sb(OH)<sub>3</sub>) exhibit amphoteric properties:

 $> Sn(OH)_2 + 2 HNO_3 \rightarrow Sn(NO_3)_2 + 2 H_2O$  $Sn(OH)_2 + 2 H^+ \rightarrow 2 H_2O + Sn^{2+}$ 

> Al(OH)<sub>3</sub> + NaOH  $\leftrightarrow$  Na[Al(OH)<sub>4</sub>]

 $Al(OH)_3 + OH^- \leftrightarrow [Al(OH)_4]^-$ 

2. Some chemical compounds, which contain p-block elements, are used as oxidizing and reducing agents in laboratorial practice. For example,  $H_2SO_4$  (con.) is a strong oxidizing agent, able to oxidize metals, non-metals and chemical compounds. The products of its reduction depend upon activity of reducing agents:

$$SO_4^{2-}$$
 + Me (IA and IIA group)  $\rightarrow$  salt +  $H_2S$ +  $H_2O$   
+ other Me  $\rightarrow$  salt +  $SO_2$  +  $H_2O$ 

 $4 \text{ Ba} + \text{H}_2\text{SO}_4 \text{ (con.)} \rightarrow 4 \text{ BaSO}_4 + \text{H}_2\text{S} \uparrow + 4 \text{ H}_2\text{O}$ 

 $HNO_3$  is a strong oxidizing agent too. Products of its reduction depend upon metal activity and concentration of the acid:

$$(con) + Me (IA and IIA group) \rightarrow salt + N_2O + H_2O$$
$$(con) + other Me \rightarrow salt + NO_2 + H_2O$$
$$(dil.) + Me (IA and IIA group) \rightarrow salt + NH_4NO_3 + H_2O$$
$$(dil.) + other Me \rightarrow salt + NO + H_2O$$

 $4 \text{ Ca} + \text{HNO}_3(\text{dilute}) \rightarrow 4 \text{ Ca}(\text{NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3 \text{ H}_2\text{O}$  $\text{Cu} + \text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2 \text{ NO}_2 \uparrow + 2 \text{ H}_2\text{O}$ 

3. Hydrolysis of salts.

An exchange reaction between water and a compound is called hydrolysis of the latter. The hydrolysis of salts is the opposite of the reaction of neutralization of weak acids (bases) with strong bases (acids) or of weak acids with weak bases. From a qualitative viewpoint, the hydrolysis of salts is the result of polarization interaction of salt ions with their hydrate shell and can be represented in a simplified fashion by the following reactions:

$$Cat^{m^{+}} + HOH \leftrightarrow CatOH^{(m^{-}1)^{+}} + H^{+}$$
$$A^{n^{-}} + HOH \leftrightarrow HA^{(n^{-}1)^{-}} + OH^{-}$$

# Hydrolysis is due to the formation of the poorly dissociating particles CatOH $^{(m-1)+}$ and HA $^{(n-1)-}$ .

The greater the charge and the smaller the radius of salt ions, the stronger is their polarization interaction with water, the weaker is the dissociation of the forming particles CatOH <sup>(m-1)+</sup> and HA<sup>(n-1)-</sup> and the greater is the extent of hydrolysis. Cations of the alkali and alkaline-earth metals, singly charged anions such as Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, and some doubly charged anions such as SO<sub>4</sub><sup>2-</sup> have only a slight polarizing effect on water molecules. In other words, salts formed by an anion of a strong acid and a cation of a strong base does not hydrolyze. The following cases of salt hydrolysis are possible: anion hydrolysis, cation hydrolysis, and simultaneous anion and cation hydrolysis.

Anion Hydrolysis. Such hydrolysis is the fate of salts formed by a cation of a strong base and an anion of a weak acid ( $K_2CO_3$ ,  $Na_2S$ ,  $Na_2SO_3$ ,  $K_3PO_4$ , etc.). Hydrolysis results in the formation of an alkaline solution (pH > 7). For example:

 $CH_3COONa \rightarrow CH_3COO^- + Na^+$ 

 $Na^+ + HOH \leftrightarrow no reaction occurs$ 

 $CH_3COO^- + HOH \text{ (or } H_2O) \leftrightarrow CH_3COOH + OH^-$ 

The molecular equation of hydrolysis is:

 $CH_3COONa + HOH \leftrightarrow CH_3COOH + NaOH$ 

This process is reversible, and the equilibrium of hydrolysis is shifted greatly to the left  $K_a(H_20) < K_a(CH_3COOH)$ .

The hydrolysis of a multicharged anion proceeds in steps in connection with the stepwise dissociation of polybasic acids, and under ordinary conditions proceeds mainly in the first step. For instance,

Na<sub>2</sub>SO<sub>3</sub>  $\rightarrow$  2 Na<sup>+</sup> + SO<sub>3</sub><sup>2-</sup> Na<sup>+</sup> + H<sub>2</sub>O  $\rightarrow$  no reaction proceeds SO<sub>3</sub><sup>2-</sup> + H<sub>2</sub>O  $\leftrightarrow$ HSO<sub>3</sub><sup>-</sup> + OH<sup>-</sup> (1st step) HSO<sub>3</sub><sup>-</sup> + H<sub>2</sub>O  $\leftrightarrow$ H<sub>2</sub>SO<sub>3</sub> + OH<sup>-</sup> (2nd step) The molecular equations are, respectively: Na<sub>2</sub>SO<sub>3</sub> + H<sub>2</sub>O  $\leftrightarrow$  NaHSO<sub>3</sub> + NaOH NaHSO<sub>3</sub> + H<sub>2</sub>O  $\leftrightarrow$ H<sub>2</sub>SO<sub>3</sub> + NaOH

**Cation Hydrolysis.** It is the fate of salts formed by a cation of a weak base and an anion of a strong acid  $[NH_4Br, ZnCl_2, Cu(N0_3)_2, etc.]$ . Hydrolysis yields an acidic solution (pH < 7). For example:

 $CuCl_2 \rightarrow Cu^{2+} + 2 Cl^{-}$ 

 $Cl^- + H_2O \leftrightarrow$  no reaction proceeds

 $Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+$ 

The molecular equation of the first step of hydrolysis is:

 $CuCl_2 + HOH \leftrightarrow CuOHCl + HC1$ 

Second step hydrolysis under ordinary conditions may be disregarded.

Anion and Cation Hydrolysis. Such hydrolysis is the fate of salts formed by a cation of a weak base and an anion of a weak acid. For example:

 $\begin{array}{l} CH_{3}COONH_{4} \rightarrow CH_{3}COO^{-} + NH_{4}^{+} \\ NH_{4}^{+} + HOH \leftrightarrow NH_{4}OH + H^{+} \\ CH_{8}COO^{-} + HOH \leftrightarrow CH_{3}COOH + OH^{-} \\ CH_{3}COO^{-} + NH_{4}^{-} + HOH \leftrightarrow CH_{3}COOH + NH_{4}OH \\ The molecular equation is: \\ CH_{3}COONH_{4} + HOH \leftrightarrow CH_{3}COOH + NH_{4}OH \end{array}$ 

Hydrolysis proceeds quite intensively in this case. The H<sup>+</sup> and OH<sup>-</sup> ions formed in hydrolysis become bound into H<sub>2</sub>O molecules, which boosts both cation and anion hydrolysis. The reaction of the solution depends on the ratio of the dissociation constants of the acids and bases formed. In the given case pH  $\approx$  7 [K<sub>b</sub> (NH<sub>4</sub>OH)  $\approx$ K<sub>a</sub> (CH<sub>3</sub>COOH)].

If an acid and a base forming a salt are not only weak electrolytes, but are also sparingly soluble or unstable and decompose with the formation of gaseous products, the hydrolysis of such salts in a number of cases is practically irreversible. This is why sulphides and carbonates of  $A1^{3+}$ ,  $Cr^{3+}$ , and  $Fe^{3+}$  cannot be obtained in an aqueous solution: 2 AlCl<sub>3</sub> + 3 Na<sub>2</sub>CO<sub>3</sub> + 3 HOH  $\rightarrow$  2 Al(OH)<sub>3</sub> + 3 CO<sub>2</sub> + 6 NaCl

The net ionic equations of hydrolysis are, respectively:

 $A1^{3+} + 3 CO_3^{2-} + 3 H_2O \rightarrow 2 A1(OH)_3 + 3 CO_2$ 

Table 5

|        | Content in       | Content in  |   |
|--------|------------------|-------------|---|
| Symbol | earth's crust, % | a human     | <b>Biological fuctions</b>  |
|        | by mass          | body        |   |
| С      | 0.14             | 16 kg/70 kg | Is a component of all-organic substances CO <sub>2</sub> is a fi- |
|        |                  | or 22.8%    | nal product of metabolic processes. Hydrocarbon buffer            |
|        |                  |             | system plays important role in acid-base status maintain-         |
|        |                  |             | ing: this system is contained in all biological fluids. The       |
|        |                  |             | following carbon containing medicines are used:                   |
|        |                  |             | $NaHCO_3$ — of gastric juice; to heal acidosis;                   |
|        |                  |             | $CO_2$ — a mixture containing 5% carbon diox-                     |
|        |                  |             | ide and 95% of oxygen is used to activate a                       |
|        |                  |             | breathing center in a human body.                                 |
|        |                  |             | Activated carbon – an adsorbent used in heal-                     |
|        |                  |             | ing heavy metals poisoning. It's also used as he-                 |
|        |                  |             | mosorbent for blood purification.                                 |
| Ν      | 0.04             | 1.8kg/70 kg | Is one of the most important bioessential chemical                |
|        |                  | or 2.6 %    | element. It's contained in amino acids, proteins, nucleic         |
|        |                  |             | acids, biological amines and some other bioactive                 |
|        |                  |             | compounds. In 1991 it was determined that nitrogen                |
|        |                  |             | monoxide NO is the only hormone gas in a human                    |
|        |                  |             | body which regulates nerve impulse transmitting in                |
|        |                  |             | brains, macrophages activation and men's sex potential.           |
|        |                  |             | The following nitrogen containing medicines are used:             |
|        |                  |             | $N_2O$ — for anastelogy. $NH_3$ — for blood ves-                  |
|        |                  |             | sels broadening and breathing center activation.                  |

**MACROELEMENTS OF p-BLOCK** 

| Symbol | Content in<br>earth's crust, %<br>by mass | Content in<br>a human<br>body | <b>Biological fuctions</b>  |
|--------|---|-------------------------------|---|
| 0      | 47.0                                      | 43kg/70 kg<br>or 61.5%        | Oxygen is a component of water and all bioactive<br>molecules. Oxygen gas is the most important<br>oxidizing agent in vivo. The decrease of oxygen<br>content in air may cause death. A new region of<br>medicine — hyperbaric oxygenation — is used for<br>activation of metabolic processes in a human body.  |
| Р      | 8.0×10 <sup>-2</sup>                      | 780g/70 kg<br>or 1.1%         | Phosphorus is an essential element for plants and<br>animals. Humans and many other creatures need<br>phosphorus to build teeth and bones. All living or-<br>ganisms use it to build their cells and to store and<br>use energy. Phosphorus is also widely used in fertil-<br>izers. For recommended daily intakes of phosphorus<br>see below. Food sources of phosphorus are dairy,<br>yogurt, fish, beef, poultry, eggs, legumes, grains: |
| S      | 5×10 <sup>-2</sup>                        | 140g/70 kg<br>or 0.2%         | is necessary to sustain bioactivity of proteins: it<br>kills bacteria, fungi and skin parasites. It can be<br>helpful in treating various cancer, food poisoning,<br>bacterial and fungal diseases, blood infections.   |
| Cl     | 1.7×10 <sup>-2</sup>                      | 95g/70 kg<br>or 0.14%         | is necessary for proper functioning of a human<br>body. Together with sodium and potassium it<br>regulates levels of cellular and intercellular elec-<br>trolytes. It has strong antibacterial properties: it is<br>also helpful in fighting cancer.  |

Table 6

## SOME MICROELEMENTS OF p-BLOCK

| Symbol | Content in<br>earth's crust, %<br>by mass | Content in<br>a human<br>body          | <b>Biological fuctions</b>   |
|--------|---|--|--|
| Al     | 8.8                                       | 0.061/70  kg                           | Neutralizes acid in stomach juices and as such is  |
|        |   | Of 8.7×10 %                            | tract. It also has anti-inflammatory properties.   |
| F      | 6.25×10 <sup>-2</sup>                     | 2.6/70 kg or<br>3.7×10 <sup>-3</sup> % | Its an important element for human health. Daily<br>intake should be about 3 mg for a healthy adult.<br>Excess of fluoride may cause osteosclerosis, calci-<br>fication and stiffness of joints, cancers of gastric<br>tract. Deficit, on the other hand, may cause tooth<br>decay, bone, joint and muscle problems. Most in-<br>dustrialized countries may have excess of fluoride<br>in the air, water and soil. |
| Br     | 1.6×10 <sup>-4</sup>                      | 0.2/70 kg or<br>2.9×10 <sup>-4</sup> % | The role of this microelement is not fully under-<br>stood yet. It acts on the nervous system and has<br>calming effect, counteracts insomnia, relieves<br>pain. It can be useful in treating various nervous<br>disorders.  |

|        | Content in         | Content in                |   |
|--------|--------------------|---------------------------|---|
| Symbol | earth's crust, %   | a human                   | Biological fuctions                                 |
|        | by mass            | body                      |   |
| Ι      | 4×10 <sup>-5</sup> | 0.013/70 kg               | Plays an important, yet not fully understood, role  |
|        |                    | or $1.9 \times 10^{-5}$ % | in human body. Up to 60% of it is located in the    |
|        |                    |                           | thyroid gland, producing hormone thyroxin and       |
|        |                    |                           | responsible for normal growth and metabolism.       |
|        |                    |                           | Unbalance in iodine level in the body may cause     |
|        |                    |                           | insomnia, sensitivity to cold, hand tremors, de-    |
|        |                    |                           | pressions, mental retardation, hair loss, unbalance |
|        |                    |                           | in body weight (either obesity or weight loss)      |
| Se     | 8×10 <sup>-5</sup> | 0.013/70 kg               | Even although its daily intake is only 0.01 mg, is  |
|        |                    | or $1.9 \times 10^{-5}$ % | necessary for proper functioning of human body.     |
|        |                    |                           | It is a strong poison in higher doses, but at the   |
|        |                    |                           | right level it prevents cancers, atherosclerosis,   |
|        |                    |                           | muscle degeneration and high blood pressure. It     |
|        |                    |                           | helps destroying bacteria, viruses and fungi.       |

#### **3.2. LABORATORY WORK**

#### «Qualitative reactions on the cations of p-block metals»

**TEST No1.** Qualitative reactions on  $NH_4^+$ 

Ammonium salts' solutions interacts with alkalis with ammonia gas elimination:

 $NH_4Cl + NaOH = NH_3 \uparrow + NaCl + H_2O$ 

Pour some drops of NH<sub>4</sub>Cl solution and add some drops of NaOH into it. Place a wet indicator paper on a test tube. What can you see?

**2.** The Nesslers' reagent is used for ammonium cation determination in aqueous solutions:

$$\mathrm{NH}_{4}\mathrm{Cl} + 2 \mathrm{K}_{2}[\mathrm{HgI}_{4}] + 4 \mathrm{KOH} \rightarrow \begin{pmatrix} \mathrm{Hg} \\ / \mathrm{NH}_{2} \\ \mathrm{O} \\ \mathrm{Hg} \end{pmatrix} \mathrm{I} \downarrow + 7 \mathrm{KI} + \mathrm{KCl} + 3 \mathrm{H}_{2}\mathrm{O}$$

Pour 2–3 drops of any ammonia salt solution into a test tube and add 1–2 drops of Nesslers' reagent. What can you see?

**TEST Nº 2**. Qualitative reactions on  $Al^{3+}$ 

Pour 5 drops of any aluminum salt solution into a test tube and add 1 drop of of NaOH solution. What can you see?

 $AlCl_3 + 3 NaOH \rightarrow Al(OH)_3 + 2 NaCl$ 

Add 5–6 drops of NaOH solution to the obtained precipitate. What can you see? Al(OH)<sub>3</sub> + NaOH  $\rightarrow$  Na[Al(OH)<sub>4</sub>]

Add 5 drops NH<sub>4</sub>Cl saturated solution. What can you see?

 $Na[Al(OH)_4] + NH_4Cl \rightarrow Al(OH)_3 \downarrow + NaCl + NH_3 \uparrow + H_2O$ 

**TEST № 3.** Qualitative reactions on Sn<sup>2+</sup>

Pour 2–3 drops of any Sn (II) salt solution into a test tube and add one drop of a NaOH up to the  $Sn(OH)_2$  precipitate formation. Dissolve the obtained precipitate in NaOH solution up to formation  $Na_2[Sn(OH)_4]$ . Add 2–3 drops of  $Bi(NO_3)_3$  solution. What can you see?

 $\begin{aligned} &\text{SnCl}_2 + 2 \text{ NaOH} \rightarrow \text{Sn}(\text{OH})_2 \downarrow + 2 \text{ NaCl} \\ &\text{Sn}(\text{OH})_2 + 2 \text{ NaOH} \leftrightarrow \text{Na}_2[\text{Sn}(\text{OH})_4] \\ &\text{Bi}(\text{NO}_3)_3 + 3 \text{ NaOH} \rightarrow \text{Bi}(\text{OH})_3 + 3 \text{ NaNO}_3 \\ &2 \text{ Bi}(\text{OH})_3 + 3 \text{ Na}_2[\text{Sn}(\text{OH})_4] \rightarrow 2 \text{ Bi} \downarrow + 3 \text{ Na}_2[\text{Sn}(\text{OH})_6] \end{aligned}$ 

**TEST Nº 4.** Qualitative reactions on  $Pb^{2+}$ 

Pour 2–3 drops of any Pb (II)salt solution into a test tube and add 2–3 drops of a KI solution What can you see?

$$Pb(NO_3)_2 + 2 KI \rightarrow PbI_2 \downarrow + 2 KNO_3$$

Dissolve the obtained precipitate in a dilute acetic acid solution under heating. Cool the obtained solution in cold water. What can you see?

**TEST № 5.** Qualitative reactions on Bi<sup>3+</sup>

Pour 2–3 drops of any Sn (II) salt solution into a test tube and add one drop of a NaOH up to the  $Sn(OH)_2$  precipitate formation. Dissolve the obtained precipitate in NaOH solution up to formation  $Na_2[Sn(OH)_4]$ . Add 2–3 drops of  $Bi(NO_3)_3$  solution. What can you see?

 $\begin{aligned} &\text{SnCl}_2 + 2 \text{ NaOH} \rightarrow \text{Sn}(\text{OH})_2 \downarrow + 2 \text{ NaCl} \\ &\text{Sn}(\text{OH})_2 + 2 \text{ NaOH} \leftrightarrow \text{Na}_2[\text{Sn}(\text{OH})_4] \\ &\text{Bi}(\text{NO}_3)_3 + 3 \text{ NaOH} \rightarrow \text{Bi}(\text{OH})_3 + 3 \text{ NaNO}_3 \\ &2 \text{ Bi}(\text{OH})_3 + 3 \text{ Na}_2[\text{Sn}(\text{OH})_4] \rightarrow 2 \text{ Bi} \downarrow + 3 \text{ Na}_2[\text{Sn}(\text{OH})_6] \end{aligned}$ 

#### Qualitative reactions on the anions of p-block nonmetals

**TEST Nº 6.** Qualitative reactions on  $\text{CO}_3^{2-}$ 

Pour 2–3 drops of any carbonate salt solution into a test tube and add 1–2 drops of HCl solution. What can you see?

 $Na_2CO_3 + 2 \text{ HCl} \rightarrow 2 \text{ NaCl} + CO_2 \uparrow + H_2O$ 

**TEST Nº 7.** Qualitative reactions on  $PO_4^{2-}$ 

Pour 4--5 drops of  $Na_2HPO_4$  solution into a test tube and add 5-7 drops of Ag- $NO_3$  solution. What can you see?

$$2 \text{ Na}_2\text{HPO}_4 + \text{AgNO}_3 \rightarrow \text{Ag}_3\text{PO}_4 \downarrow + 3 \text{ NaNO}_3 + \text{NaH}_2\text{PO}_4$$

**TEST Nº 8.** Qualitative reactions on  $B_4O_7^{2-}$ 

In the presence of concentrated sulfuric acid and ethanol borate anions form ethers which give green color to the flame:

$$Na_{2}B_{4}O_{7} + H_{2}SO_{4} + 5 H_{2}O \rightarrow Na_{2}SO_{4} + 4 H_{3}BO_{3}$$
$$H_{3}BO_{3} + 3 C_{2}H_{5}OH \rightarrow (C_{2}H_{5}O)_{3}B + 3 H_{2}O$$

Put H<sub>3</sub>BO<sub>3</sub> crystals into a porcelain cup. Add some drops of sulfuric acid and 2 mL of ethyl alcohol. Ignite a mixture.

**TEST № 9.** Qualitative reactions on Cl<sup>-+</sup>

Pour 3 drops of AgNO<sub>3</sub> solution into a test tube and add 2 drops of NaCl solution. What can you see? Add NH<sub>4</sub>OH solution up to formation a colorless solution:

$$\begin{array}{l} AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3\\ AgCl \downarrow + 2 \ NH_4OH \leftrightarrow [Ag(NH_3)_2]Cl + 2 \ H_2O\\ [Ag(NH_3)_2]Cl + KI + 2 \ H_2O \rightarrow AgI \ \downarrow + 2 \ NH_4OH + KCl \end{array}$$

Divide prepared solution into two test tubes. Add 2–3 drops of KI solution into the first test tube. What can you see? Add 5–6 drops of  $HNO_3$  solution into the second test tube. What can you see?

$$[Ag(NH_3)_2]Cl + 2 HNO_3 \rightarrow AgCl \downarrow + 2 NH_4NO_3$$

TEST № 10. Qualitative reactions on I<sup>-</sup>

Pour 2–3 drops of any Pb (II) salt solution into a test tube and add 2–3 drops of a KI solution. What can you see?

Pb (CH<sub>3</sub>COO)<sub>2</sub> + 2 KI 
$$\rightarrow$$
 PbI<sub>2</sub>  $\downarrow$  + 2 KCH<sub>3</sub>COO  
2 I<sup>-</sup> + Pb<sup>2+</sup>  $\rightarrow$  PbI<sub>2</sub>  $\downarrow$ 

**TEST № 11**. Qualitative reactions on NO<sub>3</sub><sup>-</sup>

Diphenylamine  $(C_6H_5)_2NH$  in the concentrated sulfuric acid is a reagent to determine NO<sub>3</sub><sup>-</sup> anions. What can you see?

**TEST № 12.** Qualitative reactions on NO<sub>2</sub><sup>-</sup>

**1.** Pour 4–5 drops of NaNO<sub>2</sub> solution into a test tube and add 8–10 drops of concentrated  $H_2SO_4$  solution. What can you see?

$$NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + NO_2 \uparrow + NO \uparrow + H_2O$$

Balance the equation by half-reaction method.

**2.** Pour 4–5 drops of NaNO<sub>2</sub> solution into a test tube and add 5–6 drops of dilute of  $H_2SO_4$  solution. Then add solution KMnO<sub>4</sub>solution. What can you see?

 $KNO_2 + KMnO_4 + H_2SO_4 \rightarrow KNO_3 + MnSO_4 + K_2SO_4 + H_2O$ 

Balance the equation by half-reaction method.

TEST № 13. Qualitative reactions on CH<sub>3</sub>COO<sup>-</sup>

Pour 2-3 drops of FeCl<sub>3</sub> solution into a test tube and add 1-2 drops of solution CH<sub>3</sub>COONa. What can you see?

$$3 \text{ CH}_3\text{COONa} + \text{FeCl}_3 \leftrightarrow \text{Fe}(\text{CH}_3\text{COO})_3 + 3 \text{ NaCl}$$

#### **3.3. EXCERCISES FOR THE SELF CONTROL**

**1.** Complete the following redox reactions and balance them using half-reaction method:

$$\begin{split} & KMnO_4 + Na_2SO_3 + H_2SO_4 \rightarrow \\ & HBr + H_2SO_4 \rightarrow \\ & KMnO_4 + H_2S + H_2SO_4 \rightarrow \\ & P + HNO_3 \rightarrow \end{split}$$

**2.** Define amphoteric properties. Write equations of chemical reactions, which are necessary to prove amphoteric nature of  $Pb(OH)_2$  and  $Sb(OH)_3$ .

3.Write the equations for the following salts hydrolysis:

(a)  $NaF(b) Na_2CO_3$ 

(c) Pb  $(CH_3COO)_2$  (d)  $Cr_2(SO_4)_3$ 

4.Discuss the biological functions of sulfur, nitrogen and carbon in vivo.

**5.**Explain the mechanism of buffer activity of hydrocarbonic and hydrophosphoric buffers in blood.

#### **CHAPTER 4**

#### THE d-BLOCK ELEMENTS

After reading this chapter, you should be able to:

> Derive the <u>electron configurations</u> of the d-block elements and their simple ions;

> Recall the characteristic properties of the transition elements essential to life:

(a) Their acting in Redox reactions.

(b) Their ability to form a range of complex compounds with different ligands;

(c) Their salts hydrolysis;

(d) Amphoteric character of some oxides and hydroxides containing d-block elements.

> Remember the equations of test reactions on cations of d-block elements.

#### 4.1. GENERAL CHARACTERISTICS OF D-BLOCK ELEMENTS

The d-block elements have a general electron configuration  $ns^2$  (n-1) d<sup>x</sup>, where x = 1-10. Only some elements (Cu, Ag, Au, Cr, Mo) with so called «electron jump» have the electron configuration as  $ns^1$  (n-1) d<sup>x</sup>, where x=5, 10.

The d-block elements fall in the Periodic table between the s-block and the p-block. They are often called the Transition Elements. Transition metals are strictly defined as elements with one or more stable ions which have incompletely filled d-orbitals.

| The electronic configurations for | the first row of transition elements are: |
|-----------------------------------|---|
| ElementAtomic NumberElectronic    | Configuration                             |

| C  | 01 | FA 1 2 14 2          |
|----|----|----------------------|
| Sc | 21 | $[Ar] 3d^{3}s^{2}$   |
| Ti | 22 | $[Ar] 3d^2 4s^2$     |
| V  | 23 | $[Ar] 3d^34s^2$      |
| Cr | 24 | $[Ar] 3d^{5}4s^{1}$  |
| Mn | 25 | $[Ar] 3d^54s^2$      |
| Fe | 26 | $[Ar] 3d^64s^2$      |
| Co | 27 | $[Ar] 3d^{7}4s^{2}$  |
| Ni | 28 | $[Ar] 3d^84s^2$      |
| Cu | 29 | $[Ar] 3d^{10}4s^{1}$ |
| Zn | 30 | $[Ar] 3d^{10}4s^2$   |
|    |    |                      |

In their atoms there are five separate d-orbitals each of which can accommodate two electrons of opposite spin. These five orbital have the same energy. In practice each of these orbitals must be singly occupied by an electron before pairing takes place. When all five 3d orbitals are either singly or doubly filled a degree of stability is conferred on the atom or ion. This explains the «electron jump» and electronic configurations of the atoms chromium and copper which are respectively  $3d^54s^1$  and 3d104s1. It also explains why  $Fe^{2+}$  ( $3d^6$ ) is easily oxidized to  $Fe^{3+}$  ( $3d^5$ ) but  $Mn^{2+}$  ( $3d^5$ ) is not readily oxidized to  $Mn^{3+}$  ( $3d^4$ ).

#### **Periodic Trends**

The transition elements show a horizontal similarity in their physical and chemical properties as well as the usual vertical relationship. The horizontal similarity contrasts sharply with the trend in traversing a row of the s and p block elements, e.g. Li to F, where it is the difference between them that is the most striking characteristic. This is because in the transition elements, although the nuclear charge is increasing by one, an electron is being added to an inner d-orbital. In Li to F a valency electron is being added. As an electron is being added to an inner orbital, the difference from element to element is only small. Ionization energies and electronegativities tend therefore to increase only slightly along the series.

Peculiarity of d-block elements is the absence of monotonic alteration in their atomic radii in periods and groups. This phenomenon is known as **the affect of d-contraction**: *penetration of valency d-electrons to nuclei*. For the elements with  $d^1$ ,  $d^2$  and  $d^3$  electron configuration d-contraction is highly expressed, but for  $d^9$  and  $d^{10}$  configuration - it is only negligibly expressed.



Fig. 3. Effect of d-contraction

#### **General Properties**

The transition elements are silvery metals (apart from copper). They are dense metals with high melting points and boiling points. They tend to be hard with high tensile strength and good mechanical properties. They are good conductors of heat and electricity and most have a close-packed structure of atoms. They are much less reactive than the s-block metals.

Strong forces exist between the separate atoms in a metal and these are known as metallic bonds. This can be explained by the movement of the outer shell electrons of the metal, as they move randomly throughout a lattice of regularly spaced positive ions. The moving electrons are referred to as a 'sea of electrons'. Each positively charged ion is attracted to the sea of electrons and vice versa. These electrostatic attractions bind the structure together. When a force is applied to a metal, the layers of atoms can slide over each other in a process known as slip. After slipping the atoms settle once again into a close-packed structure. This is why metals can be hammered into different shapes (malleable) or drawn into wire (ductile). In an alloy, differently sized atoms interrupt the orderly arrangement of atoms in the lattice and make it more difficult for the layers to slide over each other.

The transition elements have certain characteristic properties:

1. Form compounds in a wide variety of oxidation states,

2. Form colored compounds,

3. Form complex compounds,

4. Act as catalysts,

5. Show paramagnetism.

#### They show variable oxidation states.

Below is a table summarizing the <u>possible</u> oxidation states of the first row of transition metals: Cells highlighted in red are the most common oxidation states of each metal. It doesn't take a great deal of energy to convert from one oxidation state to another because the 4s and 3d orbitals are close together in energy. Transition metals are therefore easily oxidized and reduced and are useful as redox catalysts.

Up to manganese the highest oxidation states involve all 3d and 4s electrons. After manganese, there is a decrease in the number of oxidation states shown by each element. The lower oxidation states are found in simple ionic compounds, e.g.  $Cr^{3+}$ ,  $Mn^{2+}$ , and  $Fe^{3+}$ . The higher oxidation states give rise to covalent compounds, e.g.  $MnO_4^{-}$ ,  $Cr_2O_7^{2-}$ , or complex compounds.

#### **Chemical properties**

For d-block elements the following types of chemical reactions are typical:

Redox processes;

Salts' hydrolysis

Complex compounds formation.

Table 7

| Sc | Ti | V  | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|----|----|----|----|----|----|----|----|----|----|
| +3 | +4 | +5 | +6 | +7 | +6 | +5 | +4 | +3 | +2 |
|    | +3 | +4 | +5 | +6 | +5 | +4 | +3 | +2 |    |
|    | +2 | +3 | +4 | +5 | +4 | +3 | +2 | +1 |    |
|    | +1 | +2 | +3 | +4 | +3 | +2 | +1 |    |    |
|    |    | +1 | +2 | +3 | +2 | +1 |    |    |    |
|    |    |    | +1 | +2 | +1 |    |    |    |    |
|    |    |    |    | +1 |    |    |    |    |    |

#### VARIABLE OXIDATION STATES OF D-BLOCK-ELEMENTS

Transition metals essential to life are: Mn, Fe, Co, Cu, Zn and Mo. They are microelements which fulfill important biological properties in a human body.

#### Table 8

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| Symbol | Content in<br>a human body           | Biological fuctions  |
|--------|--------------------------------------|--|
| Ag     | $7.9 \times 10^{-4} / 70 \text{ kg}$ | Is found in human body in trace amounts and its role is not            |
| 8      | or 1.1×10 <sup>-6</sup> %            | quite understood, but it helps in memory loss and nervous ex-          |
|        |                                      | haustion. It has antibacterial properties and can also be used in      |
|        |                                      | final stages of any therapy.   |
| V      | 0.013/70 kg                          | Is used in cancer therapy as well as in treating viral, bacterial      |
|        | or 1.9×10 <sup>-5</sup> %            | and fungal diseases.   |
| W      | 0.013/70 kg                          | Is used in treating leukemia and various cancers, viral and bacterial  |
|        | or 1.9×10 <sup>-5</sup> %            | diseases. It is being tested in treating early stages of AIDS.         |
| Au     | $9.8 \times 10^{-3}$ /70 kg          | Is found in human body in trace amounts and its role is not fully      |
|        | or 1.4×10 <sup>-5</sup> %            | understood, but it is known that it helps activate immune system,      |
|        |                                      | helps in some rheumatic diseases and fighting inflammations. It        |
|        |                                      | helps in later stages of any therapy in tissue regeneration.           |
| Co     | $1.5 \times 10^{-3} / 70 \text{ kg}$ | Plays a role in stimulating blood circulation and helps in general     |
|        | or $2.1 \times 10^{6}$ %             | recuperation after sickness. The human body needs about 0.3 mg         |
|        |                                      | of cobalt daily. It is helpful in fighting cancer and anemia, lowers   |
|        | 0.010/501                            | sugar level in blood and has beneficial effect on hair growth.         |
| Mn     | 0.012/70 kg                          | Together with iron and copper, is necessary in process of              |
|        | or 1.7×10 %                          | blood production and its presence allows for correct cell de-          |
|        |                                      | velopment. Its daily intake should be about 0.2–0.3 mg per kg          |
| М.     | $0.5 \times 10^{-3} / 70.1$          | of body weight.  |
| IVIO   | $9.5 \times 10^{-50}$                | is present in numan body in trace amounts and role is not to-          |
|        | 01 1.4×10 %                          | any understood, but its lack may cause diamed, changes in              |
|        |                                      | tions caused by viruses or bacteria and in arteriosclerosis            |
| Cd     | 0.05/70.kg                           | Is very important human health as it is very dangerous and poison-     |
| Cu     | 0.03770  Kg                          | ous even in trace in amounts — it damages kidney lungs deforms         |
|        | 01 4.1×10 Kg                         | and wakens bones may cause various cancers. Even the amount of         |
|        |                                      | 1 ppm in soil causes disruption in plant growth The pendulum may       |
|        |                                      | be used for checking for cadmium in soil in the air vegetables and     |
|        |                                      | fruit. It can also destroy bacterial, fungi and molds.                 |
| Cu     | 0.072/70 kg                          | It is an important enzymes' activator, which fulfills a catalyst func- |
|        | or $1.0 \times 10^{-4}$ %            | tion in a body. It's plays an important role in blood formation.       |
| Zn     | 2.3/70 kg                            | It's contained in erythrocytes and takes part in tissues' respiration. |
|        | or $3.3 \times 10^{-3}$ %            |  |
| Fe     | 4.2/70 kg                            | It's an important component of hemoglobin and some enzymes             |
|        | or $6.0 \times 10^{-3}$ %            | (cytochrom C and others).  |
|        |                                      | It's take part in respiration and other metabolic processes. Its       |
|        |                                      | deficiency may cause anemia.   |

#### SOME MICROELEMENTS OF d – BLOCK

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#### 4.2. LABORATORY WORK «Qualitative reactions on the cations of d-block metals»

**TEST № 1**. Qualitative reactions on Cu<sup>2+</sup>

Pour 3–5 drops of  $CuSO_4$  solution into a test tube and add 1-2 drops of  $NH_4OH$  solution. What can you see?

 $2CuSO_4 + 2NH_4OH \rightarrow (CuOH)_2SO_4 \downarrow + (NH_4)_2SO_4$ 

And add 5–5 drops of of NH<sub>4</sub>OH solution. What can you see?

 $(CuOH)_2SO_4 + (NH_4)_2SO_4 + 6 NH_4OH \rightarrow 2 [Cu(NH_3)_4]SO_4 + 8 H_2O_4$ 

**TEST Nº 2.** *Qualitative reactions on*  $Ag^{++}$ 

Pour 2–3 drops of AgNO<sub>3</sub> solution into a test tube; and add 2–3 drops of HCl solution. What can you see?

$$AgNO_3 + HCl \rightarrow AgCl \downarrow + HNO_3$$

Dissolve the obtained precipitate in 5–6 drops of ammonia solution. What can you see?

$$AgCl + 2 NH_3 \leftrightarrow [Ag(NH_3)_2]Cl + 2 H_2O$$

Add 2–3 drops of HNO<sub>3</sub> solution into a test tube. What can you see?

 $[Ag (NH_3)_2]Cl + 2 HNO_3 \leftrightarrow AgCl \downarrow + 2 NH_4NO_3$ 

**TEST Nº 3.** *Qualitative reactions on*  $Zn^{2+}$ 

**1.** Pour 3–5 drops of any  $Zn^{2+}$  salt solution into a test tube and add 1–2 drops of NaOH solution. What can you see?

$$ZnCl_2 + 2 NaOH \rightarrow Zn(OH)_2 \downarrow + 2 NaCl$$

Divide an obtained precipitate into two test tubes. Add 2-3 drops of HCl solution into first test tube. What can you see? Add 5-6 drops of NaOH solution into the second test tube. What can you see?

$$Zn (OH)_2 + 2 NaOH \rightarrow Na_2[Zn(OH)_4]$$
$$Zn (OH)_2 + 2 HCl \rightarrow ZnCl_2 + 2 H_2O$$

**2.** Pour 3–5 drops of any  $Zn^{2+}$  salt solution into a test tube and add 2–3 drops of K<sub>4</sub>[Fe(CN)<sub>6</sub>] solution. What can you see?

$$3 \operatorname{ZnCl}_2 + 2 \operatorname{K}_4 [\operatorname{Fe}(\operatorname{CN})_6] \rightarrow \operatorname{K}_2 \operatorname{Zn}_3 [\operatorname{Fe}(\operatorname{CN})_6] \downarrow + 6 \operatorname{KCl}$$

**TEST Nº 4.** *Qualitative reactions on*  $Hg^{2+}$ 

**1.** Pour 3–5 drops of Hg  $(NO_3)_2$  solution into a test tube and add 2–3 drops of NaOH solution. What can you see?

Hg 
$$(NO_3)_2 + 2 NaOH \rightarrow HgO \downarrow + 2 NaNO_3 + H_2O$$

**2.** Pour 4–5 drops of Hg  $(NO_3)_2$  solution into a test tube and add 1–2 drops of KI solution. What can you see?

 $Hg (NO_3)_2 + 2 KI \rightarrow HgI_2 \downarrow + 2 KNO_3$ 

Dissolve the obtained precipitate in 5-6 drops of KI solution.

$$HgI_2 + 2 KI \leftrightarrow K_2 [HgI_4]$$

**TEST No 5.** Qualitative reactions on  $Cr^{3+}$ 

**1.** Pour 3–5 drops of any of any  $Cr^{3+}$  salt solution into a test tube solution and add 2–3 drops of NaOH solution. What can you see?

$$CrCl_3 + 3 NaOH \rightarrow Cr (OH)_3 \downarrow + 3 NaCl$$

Divide an obtained precipitate into two test tubes. Add 3–4 drops of HCl solution into the first test tube. What can you see? Add 5–6 drops of NaOH solution into the second test tube. What can you see?

 $Cr(OH)_3 + 3 HCl \rightarrow CrCl_3 + 3 H_2O$  $Cr(OH)_3 + 3 NaOH \leftrightarrow Na_3[Cr(OH)_6]$ 

**2.** Pour 2–3 drops of any of any  $Cr^{3+}$  salt solution into a test tube solution and add 2–3 drops of NaOH solution up to formation a complex compounds. Then add 3–5 drops of H<sub>2</sub>O<sub>2</sub> solution. What can you see?

$$Na_3 [Cr (OH)_6] + H_2O_2 \rightarrow Na_2CrO_4 + NaOH + H_2O_4$$

Balance the equation of a chemical reaction using a half-reaction method.

**TEST Nº 6.** *Qualitative reactions on*  $Mn^{2+}$ 

**1.** Pour 3–5 drops of any of any  $Mn^{2+}$  salt solution into a test tube and add 2–3 drops of NaOH solution. What can you see?

$$MnCl_2 + 2 NaOH \rightarrow Mn (OH)_2 \downarrow + 2 NaCl$$

Then add 3-5 drops of  $H_2O_2$  solution. What can you see?

 $Mn (OH)_2 + H_2O_2 \rightarrow MnO (OH)_2 \downarrow + H_2O$ 

**2.** Pour 1 mL of HNO<sub>3</sub> solution into a test tube and add 2-3 drops of any  $Mn^{2+}$  salt. Mix the solutions and add some crystals of NaBiO<sub>3</sub>. What can you see?

 $MnSO_4 + NaBiO_3 + HNO_3 \rightarrow HMnO_4 + Bi(NO_3)_3 + Na_2SO_4 + NaNO_3 + H_2O_3 + NaNO_3 + H_2O_3 + H_2O$ 

Balance the equation of a chemical reaction using a half-reaction method.

**TEST Nº 7.** *Qualitative reactions on*  $Fe^{2+}$ 

**1.** Prepare a solution of  $FeSO_4$  salt. Pour 2–3drops of a prepared solution into a test tube and add 2–3 drops of K<sub>3</sub> [Fe (CN) <sub>6</sub>]. What can you see?

 $\operatorname{FeCl}_2 + \operatorname{K}_3 [\operatorname{Fe} (\operatorname{CN})_6] \rightarrow \operatorname{KFe} [\operatorname{Fe} (\operatorname{CN})_6] \downarrow + 2 \operatorname{KCl}$ 

**2.** Pour 3-5 drops of FeSO<sub>4</sub> solution into a test tube and add 3-5 drops of NaOH solution. What can you see?

 $FeSO_4 + 2 NaOH \rightarrow Fe (OH)_2 \downarrow + Na_2SO_4$ 

Add 2-3 drops of  $H_2O_2$  solution. What can you see?

4 Fe (OH)<sub>2</sub> + O<sub>2</sub> + 2 H<sub>2</sub>O  $\rightarrow$  4 Fe(OH)<sub>3</sub> $\downarrow$ 

**TEST Nº 8.** *Qualitative reactions on*  $Fe^{3+}$ 

**1.** Pour 3–5 drops of any Fe<sup>3+</sup> salt solution into a test tube and add 2–3 drops of  $K_4[Fe(CN)_6]$  solution. What can you see?

$$\operatorname{FeCl}_3 + \operatorname{K}_4 [\operatorname{Fe} (\operatorname{CN})_6] \rightarrow \operatorname{KFe} [\operatorname{Fe} (\operatorname{CN})_6] \downarrow + 3 \operatorname{KCl}$$

**2.** Pour 3–5 drops of any of any  $Fe^{3+}$  salt solution into a test tube and add 3–5 drops of NaOH solution. What can you see?

$$FeCl_3 + 3 NaOH \rightarrow Fe (OH)_3 + 3 NaCl$$

**TEST Nº 9.** *Qualitative reactions on*  $Co^{2+}$ 

**1.** Pour 3–5 drops of any of any  $Co^{2+}$  salt solution into a test tube and add 1–2 drops of NaOH solution. What can you see?

 $CoCl_2 + NaOH \rightarrow CoOHCl \downarrow + NaCl$ 

Then add 3–5 drops of NaOH solution. What can you see?

 $CoOHCl + NaOH \rightarrow Co(OH)_2 \downarrow + NaCl$ 

**2.** Pour 3–5 drops of any of any  $Co^{2+}$  salt solution into a test tube and add 8–10 drops of saturated NH<sub>4</sub>CNS solution. What can you see?

$$CoCl_2 + 4 NH_4CNS \leftrightarrow (NH_4)_2[Co(CNS)_4] + 2 NH_4Cl$$

**TEST № 10.** *Qualitative reactions on* Ni<sup>2+</sup>

Pour 3–5 drops of any of any  $Ni^{2+}$  salt solution into a test tube and add 1–2 drops of NaOH solution. What can you see?

$$NiSO_4 + 2 NaOH \rightarrow Ni (OH)_2 \downarrow + Na_2SO_4$$

Dissolve the obtained precipitate in ammonia solution:

 $NiSO_4 + 6 NH_3 \leftrightarrow [Ni (NH_3)_6] SO_4$ 

#### **4.3. EXCERCISES FOR THE SELF CONTROL**

1. Complete the following redox reactions and balance them using half-reaction method:

- $\succ$  K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + NaBr + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$
- $\succ$  Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> + KOH  $\rightarrow$
- $\succ$  KM $\Pi$ O<sub>4</sub> + KNO<sub>2</sub> + KOH  $\rightarrow$
- $\succ$  FeSO<sub>4</sub> + K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$

 $\succ$  K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> + KI + HCI  $\rightarrow$ 

2. Write the electron configuration for the following atoms and ions:

(a) Cu(b) Fe<sup>2+</sup> (c) Zn<sup>2+</sup> (d) Fe<sup>3+</sup> (e) Cr(f) Co

**3.** Write reactions of hydrolysis for the following salts:

(a)FeCl<sub>3</sub> (b)  $Zn(NO_3)_2$ 

**4.** Describe the structure of the following complex ions, using VB method and crystal-field theory:

(a) $[Co(CN)_6]^{3-1}$  (b) $[CoF_6]^{3-1}$ .

## **APPENDIX 1**

## CONTENT THE CHEMICAL ELEMENTS IN A HUMAN BODY

| CHEMICAL ELEMENTS | MASS OF ELEMENTS AT<br>A NUMAN BODY OF 70 kg | PERSENT BY MASS, %   |
|-------------------|--|----------------------|
| Hvdrogen          | 7000   | 10                   |
| Lithium           | $6.7 \times 10^{-4}$                         | 1.0×10 <sup>-6</sup> |
| Beryllium         | 3.6×10 <sup>-5</sup>                         | 5.0×10 <sup>-8</sup> |
| Boron             | 0.02   | 3.0×10 <sup>-5</sup> |
| Carbon            | 16000  | 22.8                 |
| Nitrogen          | 1800   | 2.6                  |
| Oxygen            | 43000  | 61.5                 |
| Fluorine          | 2.6  | 3.7×10 <sup>-3</sup> |
| Sodium            | 100  | 0.14                 |
| Magnesium         | 19   | 0.027                |
| Aluminum          | 0.061  | 8.7×10 <sup>-5</sup> |
| Silicon           | 0.14   | 2.0×10 <sup>-4</sup> |
| Phosphorus        | 780  | 1.1                  |
| Sulfur            | 140  | 0.2                  |
| Chlorine          | 95   | 0.14                 |
| Argon             | 0.01   | 1.4×10 <sup>-5</sup> |
| Potassium         | 140  | 0.2                  |
| Calcium           | 1000   | 1.4                  |
| Scandium          | 0.013  | 2.0×10 <sup>-5</sup> |
| Titanium          | 9.0×10 <sup>-3</sup>                         | 1.3×10 <sup>-5</sup> |
| Vanadium          | 0.018  | 2.6×10 <sup>-5</sup> |
| Chromium          | 6.6×10 <sup>-3</sup>                         | 9.4×10 <sup>-6</sup> |
| Manganese         | 0.012  | 1.7×10 <sup>-5</sup> |
| Iron              | 4.2  | $6.0 \times 10^{-3}$ |
| Cobalt            | $1.5 \times 10^{-3}$                         | 2.1×10 <sup>-6</sup> |
| Nickel            | 0.01   | 1.4×10 <sup>-5</sup> |
| Copper            | 0.072  | $1.0 \times 10^{-4}$ |
| Zinc              | 2.3  | 3.3×10 <sup>-3</sup> |
| Gallium           | 1.6×10 <sup>-5</sup>                         | 2.3×10 <sup>-8</sup> |
| Germanium         | 4.3×10 <sup>-6</sup>                         | 6.2×10 <sup>-9</sup> |
| Arsenic           | 0.018  | 2.6×10 <sup>-5</sup> |
| Selenium          | 0.013  | 1.9×10 <sup>-5</sup> |
| Bromine           | 0.2  | 2.9×10 <sup>-4</sup> |
| Rubidium          | 0.68   | 9.7×10 <sup>-4</sup> |
| Strontium         | 0.32   | 4.1×10 <sup>-4</sup> |
| Zirconium         | 0.42   | 7.0×10 <sup>-4</sup> |
| Niobium           | 0.11   | 1.6×10 <sup>-4</sup> |
| Molybdenum        | 9.5×10 <sup>-3</sup>                         | 1.4×10 <sup>-5</sup> |
| Silver            | 7.9×10 <sup>-4</sup>                         | 1.1×10 <sup>-6</sup> |
| Cadmium           | 0.05   | 4.1×10 <sup>-5</sup> |
| Tin               | 0.017  | 2.4×10 <sup>-5</sup> |
| Antimony          | 0.32   | 4.1×10 <sup>-4</sup> |
| Tellurium         | $8.2 \times 10^{-3}$                         | $1.2 \times 10^{-5}$ |

| CHEMICAL ELEMENTS | MASS OF ELEMENTS AT<br>A NUMAN BODY OF 70 kg | PERSENT BY MASS, %    |
|-------------------|--|-----------------------|
| Iodine            | 0.013  | $1.9 \times 10^{-5}$  |
| Cesium            | $1.5 \times 10^{-3}$                         | 2.1×10 <sup>-6</sup>  |
| Barium            | 0.022  | 3.1×10 <sup>-5</sup>  |
| Gold              | 9.8×10 <sup>-3</sup>                         | 1.4×10 <sup>-5</sup>  |
| Mercury           | 0.013  | 1.9×10 <sup>-5</sup>  |
| Lead              | 0.12   | $1.7 \times 10^{-4}$  |
| Bismuth           | 2.3×10 <sup>-4</sup>                         | 3.3×10 <sup>-7</sup>  |
| Radium            | 3.1×10 <sup>-11</sup>                        | $4.4 \times 10^{-14}$ |
| Uranium           | 9.0×10 <sup>-5</sup>                         | $1.3 \times 10^{-7}$  |

#### **APPENDIX 2**

### THE FORMATION CONSTANT

| Complex ion  | K <sub>f</sub>         | Complex ion  | K <sub>f</sub>         |
|--|------------------------|--|------------------------|
| $[Ag(CN)_2]^-$   | 1.41×10 <sup>-20</sup> | $[CdI_4]^{2-}$   | 7.9×10 <sup>-7</sup>   |
| $\left[\operatorname{Ag}(\operatorname{NH}_3)_2\right]^+$    | 5.75×10 <sup>-8</sup>  | $[Cd(CN)_4]^{2-}$  | 7.76×10 <sup>-18</sup> |
| $[Ag(NO_2)_2]^2$   | 1.48×10 <sup>-3</sup>  | $[Cu(NH_3)_4]^{2+}$  | 9.33×10 <sup>-13</sup> |
| [Ag(NCS) <sub>2</sub> ] <sup>-</sup>                         | 5.37×10 <sup>-9</sup>  | $\left[\operatorname{Cu}(\operatorname{NCS})_{4}\right]^{2}$ | 3.02×10 <sup>-7</sup>  |
| $[Ag(S_2O_3)_2]^{3-1}$                                       | 3.47×10 <sup>-14</sup> | $[Co(NH_3)_4]^{2+}$  | 4.07×10 <sup>-5</sup>  |
| $[Au(CN)_2]^-$   | 5.0×10 <sup>-39</sup>  | $[Co(NH_3)_6]^{2+}$  | 8.51×10 <sup>-6</sup>  |
| $[Bi(NCS)_6]^{3-}$   | 5.89×10 <sup>-5</sup>  | $[Co(CN)_6]^{4-}$  | 8.13×10 <sup>-20</sup> |
| $[Cd(NH_3)_4]^{2-}$  | 2.88×10 <sup>-7</sup>  | $[Co(NCS)_4]^{2}$  | 6.31×10 <sup>-3</sup>  |
| $[CdBr_4]^{2-}$  | 1.17×10 <sup>-3</sup>  | $[Co(NH_3)_6]^{3+}$  | 6.17×10 <sup>-36</sup> |
| $[Co(CN)_{6}]^{3-}$  | 1.0×10 <sup>-64</sup>  | $[PbBr_4]^{2-}$  | 1.0×10 <sup>-3</sup>   |
| $\left[\operatorname{Cr}(\operatorname{NCS})_{6}\right]^{3}$ | 1.58×10 <sup>-4</sup>  | $[PbI_4]^{2-}$   | 6.0×10 <sup>-7</sup>   |
| $[Fe(CN)_6]^{4-}$  | 1.0×10 <sup>-24</sup>  | $[Pb(NCS)_4]^{2}$  | 0.14                   |
| $[Fe(CN)_6]^{3-}$  | 1.0×10 <sup>-31</sup>  | $[Pb(S_2O_3)_4]^{6-}$  | 6.31×10 <sup>-8</sup>  |
| $[Fe(NCS)_6]^{3-}$   | 5.89×10 <sup>-4</sup>  | $[PbCl_4]^{2-}$  | 0.1                    |
| $[HgBr_4]^{2}$   | 1.0×10 <sup>-21</sup>  | $[PbBr_4]^{2-}$  | 7.9×10 <sup>-14</sup>  |
| $[Hg(CN)_4]^{2-}$  | 3.1×10 <sup>-42</sup>  | $[PtCl_4]^{2-}$  | $1.0 \times 10^{-16}$  |
| $[HgCl_4]^{2-}$  | 8.5×10 <sup>-16</sup>  | $[PtBr_4]^{2-}$  | 3.0×10 <sup>-21</sup>  |
| $[Hg(NH_3)_4]^{2-}$  | 5.0×10 <sup>-20</sup>  | $[Zn(NH_3)_4]^{2+}$  | 2.0×10 <sup>-9</sup>   |
| $\left[\mathrm{HgI}_{4}\right]^{2}$                          | 051×10 <sup>-30</sup>  | $[ZnCl_4]^{2-}$  | 10                     |
| $\left[\mathrm{Hg}(\mathrm{NCS})_4\right]^{2-1}$             | 1.7×10 <sup>-20</sup>  | $[ZnBr_4]^{2}$   | 316.2                  |
| $[Mn(C_2O_4)_3]^{3-}$  | 3.8×10 <sup>-20</sup>  | $\left[\operatorname{Zn}(\operatorname{CN})_{4}\right]^{2}$  | $1.0 \times 10^{-19}$  |
| $\left[\mathrm{Ni}(\mathrm{CN})_4\right]^{2-}$               | 1.0×10 <sup>-31</sup>  | $\left[\operatorname{Zn}(\operatorname{NCS})_{4}\right]^{2}$ | 2.0×10 <sup>-4</sup>   |
| $\left[\mathrm{Ni}(\mathrm{NH}_3)_4\right]^{2+}$             | 3.4×10 <sup>-8</sup>   |  |                        |

#### GLOSSARY

Aluminum neutralizes acid in stomach juices and as such is used to control heartburn and ulcers in gastric tract. It also has anti-inflammatory properties.

Antimony (Sb) — its role in human body is not fully known yet except that it plays a role in metabolism. It is useful in treating cancers and bacterial and viral diseases. It is being tested for early stages of AIDS.

**Bismuth** is one of the microelements found in human body that its role is not fully understood. It has antibacterial properties and is used mainly in treating diarrhea and inflammations of intestines.

**Bromine** — the role of this microelement is not fully understood yet. It acts on the nervous system and has calming effect, counteracts insomnia, relieves pain. It can be useful in treating various nervous disorders.

**Cadmium** is very important to human health as it is very dangerous and poisonous, even in trace amounts — it damages kidneys, lungs, deforms and weakens bones, may cause various cancers. Even the amount of 1 ppm in soil causes disruption in plant growth. The pendulum may be used for checking for cadmium in soil, in the air, vegetables and fruit. It can also destroy bacteria, fungi and molds.

**Calcium** is the main building block in bones and its daily intake for a healthy adult is about 1 g (1.5–2 g for teens and pregnant women). Calcium together with magnesium relieves tiredness, headache and insomnia in case of high lead concentration (e.g. pollution from car exhaust). It helps in heart problems, TB and tooth problems.

**Chlorine** is necessary for proper functioning of a human body. Together with sodium and potassium it regulates levels of cellular and intercellular electrolytes. It has strong antibacterial properties; it is also helpful in fighting cancer.

**Chromium** in proper levels is necessary in human body. Excess in the body may increase the risk of lung cancer and excess in the air may cause asthma. Deficit of chromium may disrupt metabolism as it controls assimilation of carbohydrates; it may also be responsible for cataract. Chromium helps in treating arteriosclerosis, diabetes, fighting some cancers (especially of pancreas), viruses,. Fluoride is an important element for human health. Daily intake should be about 3 mg for a healthy adult. Excess of fluoride may cause osteosclerosis, calcification and stiffness of joints, cancers of gastric tract. Deficit, on the other hand, may cause tooth decay, bone, joint and muscle problems. Most industrialized countries may have excess of fluoride in the air, water and soil.

**Cobalt** plays a role in stimulating blood circulation and helps in general recuperation after sickness. The human body needs about 0.3 mg of cobalt daily. It is helpful in fighting cancer and anemia, lowers sugar level in blood and has beneficial effect on hair growth.

**Coordinate covalent bond**: A bond formed between a Lewis base and a Lewis acid by sharing an electron pair originally belonging to the Lewis base.

**Coordinate:** Use of a lone pair to form a coordinate covalent bond.

**Coordination compound:** A compound in which a metal ion or atom is bonded to one or more molecules or anions so as to define an integral structural unit.

#### **Coordination number:**

**Crystal field:** The electrostatic influence of the ligands (modeled as negative point charges) on the central ion of a complex.

Degenerate: Having the same energy, as in orbitals.

**Gold** is found in human body in trace amounts and its role is not fully understood, but it is known that it helps activate immune system, helps in some rheumatic diseases and in fighting inflammations. It helps in later stages of any therapy in tissue regeneration.

**Iodine** plays an important, yet not fully understood, role in human body. Up to 60% of it is located in the thyroid gland, producing hormone thyroxine and responsible for normal growth and metabolism. Unbalance in iodine level in the body may cause insomnia, sensitivity to cold, hand tremors, depressions, mental retardation, hair loss, unbalance in body weight (either obesity or weight loss).

Ligand: A group attached to a central metal ion in a complex.

**Lithium**, even although its role in human body is not well known yet, makes a big difference in our well-being. Its deficit causes abnormalities in brain development, various mental disorders, like depression or aggression. It is being tested in treating alcohol and drug dependencies.

**Magnesium** is necessary for proper functioning of a human body and its daily intake should be about 10 mg for every kg of body weight. It helps preventing illness by increasing body's own defense system. Deficit of magnesium may create problems with nervous system, heart, blood circulation, muscles, may cause arteriosclerosis, anemia, leukemia and other diseases. It may also cause dizziness, hair loss, morning tiredness and sexual problems.

**Manganese**, together with iron and copper, is necessary in process of blood production and its presence allows for correct cell development. Its daily intake should be about 0.2–0.3 mg per kg of body weight.

**Molybdenum** is present in human body in trace amounts and its role is not totally understood, but its lack may cause diarrhea, changes in sexual glands, tooth decay. It is helpful in fighting inflammations caused by viruses or bacteria and in arteriosclerosis.

**Octahedral complex**: A complex in which six ligands are arranged at the corners of a regular octahedron with the metal atom at the center

**Phosphor** is a macroelement that is a building block of a human body — in bones and teeth as well as various anabolic and catabolic processes. Its daily intake should be about 400 mg. In therapy, together with calcium, magnesium and silica, it prevents osteoporosis and spinal deformations.

**Potassium,** together with chlorine and sodium, regulates the level of cellular and intercellular electrolytes. Its deficit may create very serious health risks — disturbances in heart beat, muscle cramps, nervous disorders. The daily intake should be about 2–4 g.

**Selenium**, even although its daily intake is only 0.01 mg, is necessary for proper functioning of human body. It is a strong poison in higher doses, but at the

right level it prevents cancers, arteriosclerosis, muscle degeneration and high blood pressure. It helps destroying bacteria, viruses and fungi.

**Silica** is found in most parts of human body and its deficit may create various health problems, like hair loss, brittle fingernails, various inflammations, skin and gum problems. It plays an important role in fighting cancers, in cellular regeneration, especially bone cells.

**Silver** is found in human body in trace amounts and its role is not quite understood, but it helps in memory loss and nervous exhaustion. It has antibacterial properties and can also be used in final stages of any therapy.

**Sodium** together with potassium and chlorine manages cellular and intercellular electrolyte balance. Its daily intake depends on the environment — temperature, humidity, as well as age and activities of a person, and it varies from 2–4 g. (So-dium is lost through perspiratory glands.) It controls proper osmotic pressure and pH balance in the body. Excess is harmful in bad circulation and hypertension.

**Square planar complex**: A complex in which four ligands lie at the corners of a square with the metal atom at the center.

**Sulfur** is necessary to sustain bioactivity of proteins; it kills bacteria, fungi and skin parasites. It can be helpful in treating various cancers, food poisoning.

**Tetrahedral complex**: A complex in which four ligands lie at the corners of a regular tetrahedron with the metal atom at the center.

**Vanadium** is used in cancer therapy as well as in treating viral, bacterial and fungal diseases.

**Wolfram** is used in treating leukemia and various cancers, viral and bacterial diseases. It is being tested in treating early stages of AIDS.

#### LITERATURE

1. Chang Raymond. Chemistry: 4 th ed.

2. Leo J. Malone. Basic concepts of chemistry: 4 th ed.

3. Atkins P. W., Jones L. L. Chemistry: Molecules, Matter, and Change, 3 rd ed. W. H. Freeman and Company: New York, 1997, Chapter 21.

4. Huheey J. E., Keiter E. A., Keiter R. L. Inorganic Chemistry: Principles of Structure and Reactivity, 4 th ed. Harper Collins College Publishers: New York, 1993, Chapter 11.

5. Shriver D. F., Atkins P., Langford C. H. Inorganic Chemistry, 2 nd ed. W. H. Freeman and Company: New York, 1994, Chapter 6.

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Учебное издание

# ХИМИЯ ЭЛЕМЕНТОВ (на английском языке)

Учебное пособие для лабораторно-практических занятий к курсу по общей химии для студентов лечебного факультета, обучающихся на английском языке

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