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В учебном пособии изложены теоретические вопросы и приведены методики выполнения лабораторных работ. Для организации самостоятельной работы студентов представлены задачи и тестовые задания. В конце учебного пособия даны необходимые справочные материалы и словарь важнейших физико-химических терминов.

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CHAPTER 13

ELECTRONIC STRUCTURE OF ATOMS

> *Today I have made a discovery*
> *as important as that of Newton.*
> *Max Planck speaking to his son in 1900*

After reading this chapter, you should be able to:

- define the main steps in the development of atomism;
- define atomic orbitals, their shapes and energies with the help of the system of quantum numbers;
- be able to represent electronic configuration of atoms;
- discuss the Pauli's exclusion principle and Hund's rule;
- discuss the following physiochemical properties of atoms: atomic radius, ionization energy, electron affinity and electronegativity.

Thus far, we have focused on the bulk properties of matter. Thermodynamics and chemical kinetics provide important information regarding chemical processes, but they do not explain what takes place at the molecular level during these processes. Now we shall take a close look at the properties of atoms and molecules. In this chapter, we briefly describe the development of atomic theory (atomism) and discuss the quantum mechanical model of an atom.

13.1. The development of atomic theory

Atomism is a branch of science dealing with atomic structure and its properties. It has a long history. In the 5th century B. C. the Greek philosopher Democritus expressed the belief that all matter is composed of very small indivisible particles, which he named atoms. The atoms themselves remain unchanged, but move about in space to combine in various ways to form all macroscopic objects. Early atomic theory stated that the characteristics of an object are determined by the shape of its atoms. So, for example, sweet things are made of smooth atoms, bitter things are made of sharp atoms (figure 13.1).

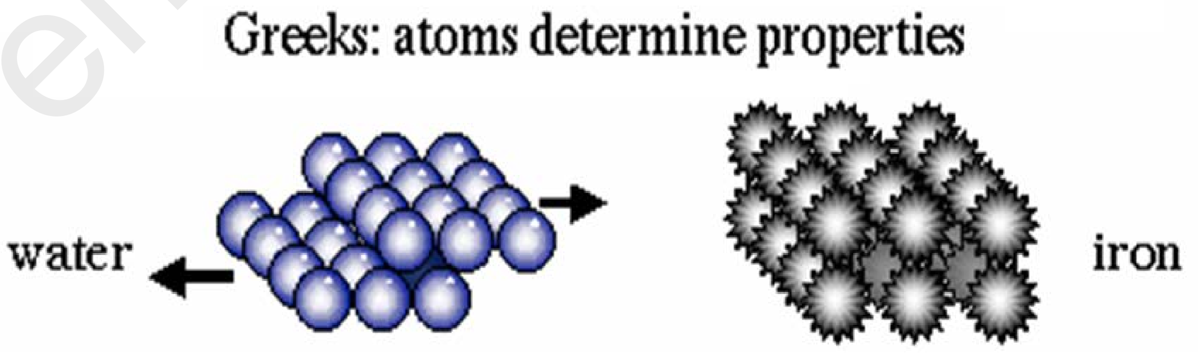


Figure 13.1 — The models of atoms, developed by ancient Greeks

Democritus (around 460 to 370 BC), philosopher from Greece, is considered the founder of *atomism*. He regarded atoms as imperceptible, individual particles that differ only in shape and position. He maintained the impossibility of dividing things *ad infinitum*. He supposed the atoms, which are originally similar, to be impenetrable and have a density proportionate to their volume.

The further development of atomism we find in J. Dalton's and M. Lomonosov's atomic theories (XVIII–XIX centuries). They defined an atom as a basic unit of an element that can enter into chemical combination. It was John Dalton, in the early 1800's, who determined that each chemical element is composed of a unique type of atoms, and that the atoms differed by their masses. He devised a system of chemical symbols and, having ascertained the relative weights of atoms, arranged them into a table. In addition, he formulated the theory that a chemical combination of different elements occurs in simple numerical ratios by weight, which led to the development of the laws of definite and multiple proportions (Figure 13.2).

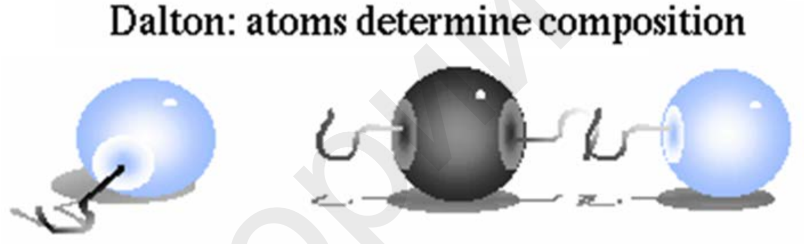


Figure 13.2 — Dalton model of atoms

John Dalton (1766–1844) English meteorologist and chemist, a pioneer in the development of modern atomic theory. He was the first to measure atomic weight of chemical elements. He studied mixed gases and the expansion of gases under heat. Dalton's Law is still used to describe the law of partial pressures in chemistry.

M. Lomonosov (1711–1765) is the great Russian scientist who contributed a lot into the development of chemistry, physics, mineralogy, and astronomy. He developed the Law of Mass Conservation and formulated atomic-molecular doctrine.

The next step in the development of atomism was creating physical models that reflected the complex structure of atoms.

In 1911, Ernest Rutherford developed the planetary (figure 13.3) model of the atom that was the first coherent explanation of the structure of an atom. Using alpha particles emitted by radioactive atoms, he showed that the atom consists of a central, positively charged core, the nucleus, and negatively charged particles called electrons that orbit the nucleus. There was one serious obstacle to acceptance of the nuclear atom, however. According to classical theory, as the electrons orbit about the nucleus, they are continuously being accelerated, and all accelerated charges radiate electromagnetic energy. Thus, they should lose their energy and spiral into the nucleus.

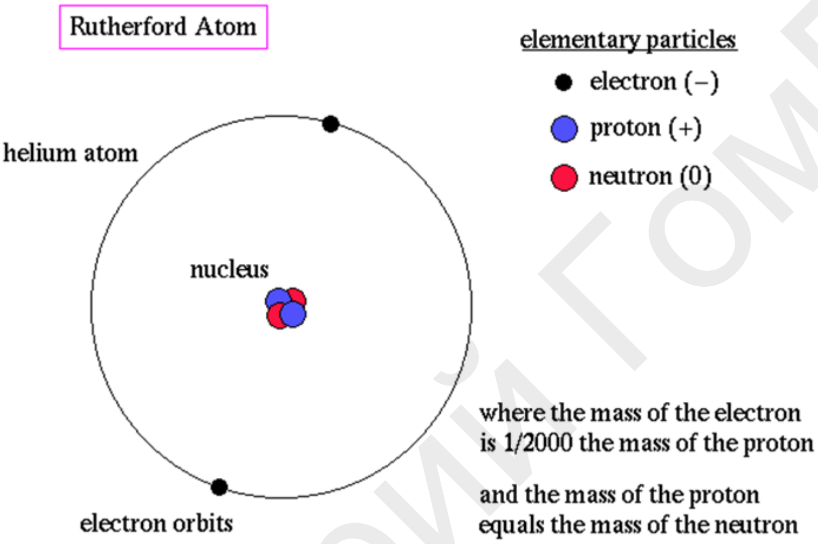


Figure 13.3 — Rutherford model of the atom

Ernest Rutherford (1871–1937) was a professor at the Universities of Cambridge and of Manchester. His importance comes after the discovery of radioactivity; he identified the components of radioactivity: alpha, beta, and gamma particles. He was the first one to discover the true structure of an atom, it having a central nucleus with an electron cloud surrounding it. Rutherford was the Nobel Prize winner in Chemistry 1908 «for his investigations into the disintegration of the elements, and the chemistry of radioactive substances».

This difficulty was solved by Niels Bohr (1913), who applied the quantum theory developed by Max Planck and Albert Einstein to the problem of atomic structure. Bohr proposed that electrons could circle a nucleus without radiating energy only in orbits for which their orbital angular momentum was an integral multiple of Planck's constant h divided by 2π. The discrete spectral lines emitted by each element were produced by electrons dropping from allowed orbits of higher energy to those of lower energy, the frequency of the photon of light emitted being proportional to the energy difference between the orbits.

Niels (Henrik David) Bohr (1885–1962) was a Danish physicist who made fundamental contributions to understanding atomic structure and quantum mechanics. Bohr is widely considered one of the greatest physicists of the twentieth century. He won the Nobel Prize in physics in 1922 for his theory on atomic structure (also known as the Quantum Theory), which was published in papers between 1913 and 1915.

Bohr model (figure 13.4) shows electrons circling the nucleus at different levels or orbitals much like planets circle the sun. Electrons move from one energy state to another but can only exist at definite energy levels. The energy absorbed or released when electrons change states is in the form of electromagnetic radiation.

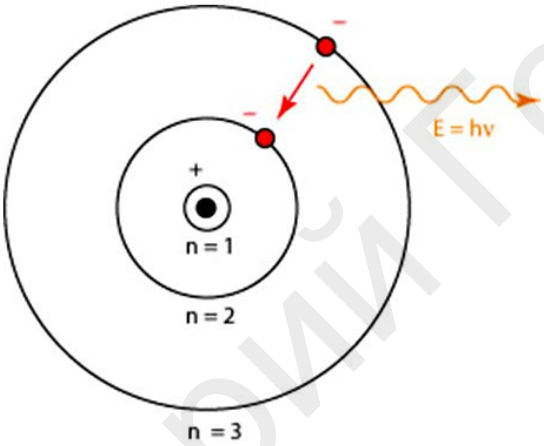


Figure 13.4 — Bohr model of the atom

Around the same time, experiments on X-ray spectra by H. G. J. Moseley showed that each nucleus was characterized by an atomic number, equal to the number of unit positive charges associated with it. By rearranging the periodic table according to atomic number rather than atomic weight, a more systematic arrangement was obtained. The development of quantum mechanics during the 1920s resulted in a satisfactory explanation for all phenomena related to the role of electrons in atoms and all aspects of their associated spectra. With the discovery of the neutron in 1932 the modern picture of the atom was complete.

13.2. The modern atomic theory

Bohr model was only able to explain the simplest atoms, like hydrogen. A modern day theory is based on mathematics and the properties of waves. The wave model forms the basis for the **Quantum Theory.** This theory gives the probability of locating electrons in a particular location, unlike assuming electrons orbit the nucleus as in the Bohr model. **Quantum Mechanics is a branch of physics** dealing with motion of elementary particles.

Atom is a micro system composed of a positively charged nucleus and negatively charged electron shell.

Atomic nucleus is a positively charged particle composed of protons, neutrons and some other elementary particles. 99.95 % of atomic mass of is stored in its nucleus (table 13.1). Elementary particles are joined together by nucleus forces which are much stronger than forces of electrostatic repulsion.

Table 13.1 — Characteristics of the Elementary Particles Contained in an Atom

Particle	**Symbol**	**Rest mass**		**Charge**	
		absolute, kg	relative, amu	electric, C	relative
Proton	p	1.673×10^{-27}	1.007 276	1.602×10^{-19}	+1
Neutron	n	1.675×10^{-27}	1.008 665	0	0
Electron	e	9.109×10^{-31}	0.000 549	1.602×10^{-19}	–1

Atomic number (N) is a fundamental characteristic of an atom. It is equal to the number of protons in atomic nucleus and its electric charge. Mass number (A) is equal to the number of protons (the charge of the nucleus or its atomic number) Z plus the number of neutrons N:

$$A = Z + N \tag{13.1}$$

A chemical element is a type of atoms with the same atomic number. All matter consists of these elements and as of 2007, 118 elements have been discovered or artificially created. 94 elements occur naturally on Earth.

Isotopes (Greek *isos* is «equal», *tópos* is «site, place») are any of the different types of atoms of the same chemical element, each having a different atomic mass (mass number). Isotopes of an element have nuclei with the same number of protons (the same atomic number) but different numbers of neutrons. Therefore, isotopes have different mass numbers, which give the total number of protons plus neutrons.

Most chemical elements are composed of several isotopes. For example, Hydrogen is composed of three isotopes (table 13.2 and figure 13.5).

Table 13.2 — Hydrogen Isotopes

Isotope	**Symbol**	**Number of p**	**Number of n**
Protium	H	1	0
Deuterium	D	1	1
Tritium	T	1	2

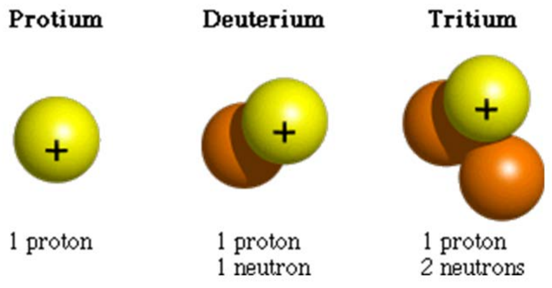


Figure 13.5 — The nuclei of the three isotopes of hydrogen

Isotopes are specified by the name of the particular element, implicitly giving the atomic number, followed by a hyphen and the mass number (e.g. helium-3, carbon-12, carbon-13, iodine-131 and uranium-238). In symbolic form, the number of nucleons is denoted as a superscripted prefix to the chemical symbol (e.g. ^{3}He, ^{12}C, ^{13}C, ^{131}I and ^{238}U).

About 339 isotopes occur naturally on Earth, of which 256 (about 75 %) are stable (or, have never been observed to decay; this note is necessary because many «stable» isotopes are predicted to be radioactive with very long half-lives). Counting the radioactive nuclides not found in nature that has been created artificially, more than 3100 nuclides are currently known.

Nucleus stability depends upon its **neutron-proton ratio** (N/Z). It was proved that for stable light elements a ration N/Z equals to unity, and for unstable ones $N/Z > 1$. For stable heavy elements $N/Z < 1.5$, and for unstable ones $N/Z > 1.5$. The chart of stable and unstable isotopes is represented in figure 13.6.

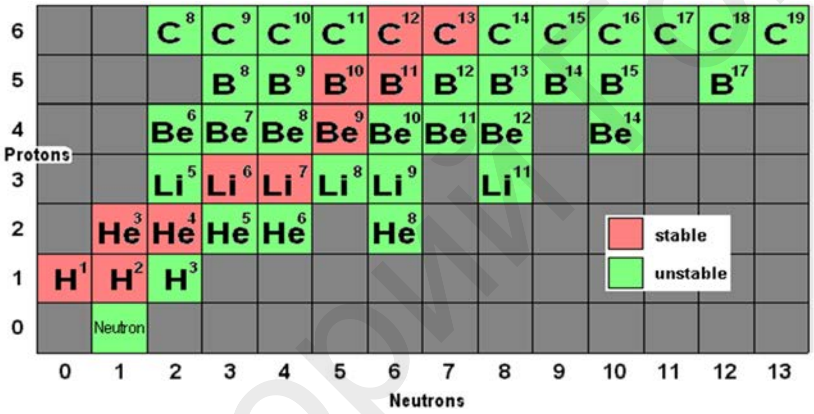


Figure 13.6 — Chart of Nuclear Isotopes

Being incorporated in a human body radioisotopes disturb normal biochemical reactions and suppress immune system. They are responsible for numerous diseases of people. There is a hypothesis that a human body protects itself from radiation selectively absorbing elements from the surroundings. Stable isotopes have the priority. Stable isotopes prevent accumulation of radioactive elements in a human body. The stable isotopes that block accumulation of radioactive analogues are given in the table 13.3.

It was proved that intake of a blocking doze of stable iodine equal to ~ 100 mg, before two hours after I-131 accumulation, decreases incorporation of radioactive iodine in thyroid gland by 90 %.

Table 13.3 — The stable isotopes that block accumulation of radioactive analogues

Stable isotopes	Radioactive isotopes
Ca-40	Sr-90
K-39	Cs-137
I-137	I-131
Fe-56	Pu-238,239

Nowadays radioactive isotopes are applied in different branches of medicine: to diagnose various diseases, to treat oncological diseases, and for pathophysiological investigations.

Medical physics is a branch of physics applied to medicine and biology and is an expanding field as a separate discipline. Applications of physics in medicine cover a wide range among which the use of radioisotopes and X rays in cancer treatment, and functional studies of organs using sophisticated data processing systems are a few to list (figure 13.7).

Figure 13.7 — Important developments in Medical Physics hold promise for application of high technology to patient care

13.3. Electronic structure of atoms

All chemical reactions proceed with changing in electronic configuration of atoms involved into a process. The electron (ē) is an elementary particle, discovered in 1897 by J. J.Thompson at Cambridge University, while he was studying cathode ray tubes.

The main postulate of quantum mechanics declares that the position of the electron in the atom is completely unpredictable. According to the Heisenberg uncertainty principle the exact momentum and position of the electron cannot be simultaneously determined. Quantum mechanics does not attempt to establish the exact position of an electron in atom, but is concerned with the probability of its being found in the space around the nucleus. Atomic orbital *(AO)* is the area of space around the nucleus characterized by high probability to find electron in it (no less than 90 %).

The orbital of each electron in an atom can be described by a wave function (ψ). ψ^2dV is a probability of locating the electron in elementary volume dV. The radial distribution of probability to find an electron looks like a wave (figures 13.8 and 13.9).

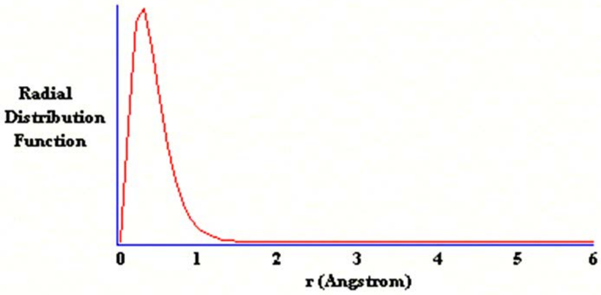


Figure 13.8 — Plot of radial distribution function for 1s-electron versus radius

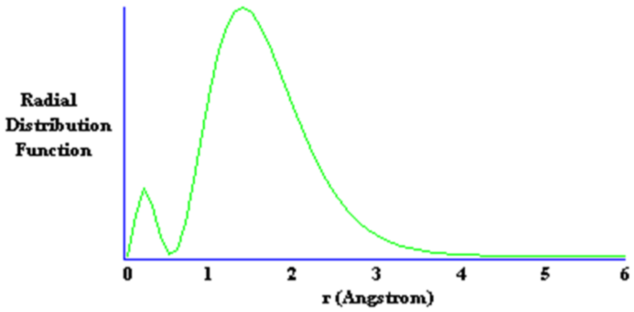


Figure 13.9 — Plot of radial distribution function for 2s-electron versus radius

An orbital can be represented as a short horizontal line or a square: (__ or ☐).

As with all elementary particles, electrons can act as particles and also as waves. This phenomenon is called the **wave-particle duality**. De Broglie deduced that the particle and wave properties are related by the expression:

$$\lambda = h / m \times \upsilon, \qquad (13.2)$$

where λ — wavelength; m — mass of the electron; υ — its velocity.

13.4. Quantum numbers

The energy state of electrones is defined with the help of four quantum numbers.

The principal quantum number (n) can have integral values 1, 2, 3, 4 and some forth. It determines the total energy of an orbital and also relates to the average distance of the electron from the nucleus in a particular orbital. A collection of orbitals with the same value of n is called an electron shell. The larger the n, the greater the energy of an orbital and the greater the average distance of an electron in the orbital from the nucleus (figure 13.10).

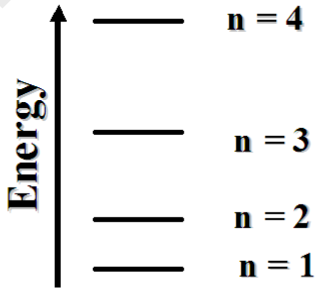


Figure 13.10 — Energy diagram of electron shells

The angular momentum (orbital) quantum number (ℓ) takes the integral values from 0 to (n-1). It determines the shape of the orbital and a number of subshells within a shell. The orbitals with the same n and ℓ values are referred to as a **subshell**. When n = 1, there is only one possible value of ℓ; that is, $\ell = n - 1 = 1 - 1 = 0$. When n = 2, there are two values of ℓ, given by 0 and 1. When n = 3, there three values of ℓ, given by 0, 1, and 2. The value of ℓ is generally designated by the letters s, p, d … as follows.

ℓ	0	1	2	3	4
Name of Subshell	s	p	d	f	g

Thus when $\ell = 0$, we have an s orbital; if $\ell = 1$, we have a p orbital, and so on. The unusual sequence of letters (s, p, and d) has a historical origin.

The magnetic quantum number (m_ℓ) describes orientation of the orbital in space and a number of orbitals within a subshell. For a certain subshell m_ℓ takes all integer values from $-\ell$ up to $+\ell$ ($-\ell \dots 0 \dots +\ell$). For s-subshell ($\ell = 0$) $m_\ell = 0$, thus there is only one s-orbital in the s-subshell. For p-subshell ($\ell = 1$) $m_\ell = -1, 0, +1$, thus there are three p-orbitals within the p-subshell.

For d-subshell ($\ell = 3$) $m_\ell = -2, -1, 0, +1, +2$, thus there are five d-orbitals within the d-subshell. For f-subshell ($\ell = 4$) $m_\ell = -3, -2, -1, 0, =+1, +2, +3$, thus there are seven f-orbitals within the f-subshell.

The electron spin quantum number (m_s) characterizes two possible spinning motions of an electron, one clockwise and the other counter clockwise. It takes the value of +½ and -½. (figure 13.11).

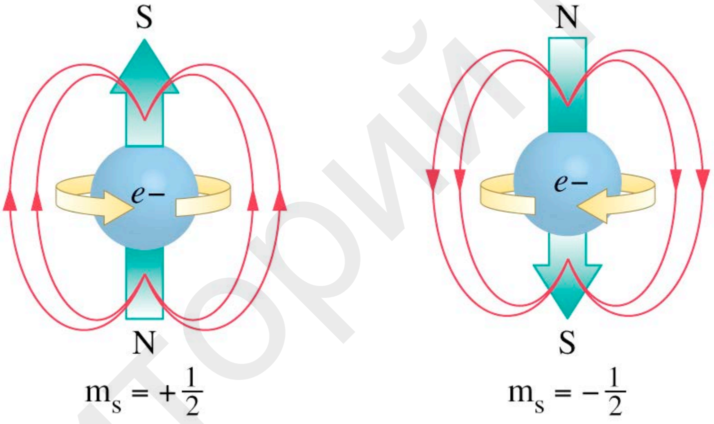


Figure 13.11 — Two possible spinning motions of an electron

13.5. Atomic orbitals

Quantum numbers enable us to discuss atomic orbitals in atoms more fully. Table 13.4 shows the relation between quantum numbers and atomic orbitals.

Table 13.4 — Relation between quantum numbers and atomic orbitals

n	ℓ	m_ℓ	Number of orbitals	Atomic orbital designations
1	0	0	1	1s
2	0	0	1	2s
	1	-1, 0, +1	3	$2p_x$, $2p_y$, $2p_z$
3	0	0	1	3s
	1	-1, 0, +1	3	$3p_x$, $3p_y$, $3p_z$
	2	-2,-1, 0, +1,+2	5	$3d_{xy}$, $3d_{yz}$,$3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$

s Orbitals

It should be clear that the s orbitals start with the principle quantum number n = 1. If n = 1, then the angular quantum number ℓ can assume only the value of zero; therefore, there is only one s orbital. The contour diagram for an s orbital is shown in figure 13.12. All s orbitals are spherical and increase in the size with increasing **n.**

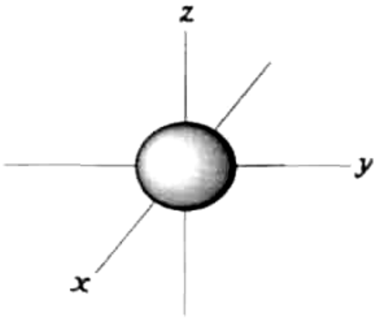


Figure 13.12 — The contour diagram for an s orbital

p Orbitals

The p orbitals start with the principle quantum number n = 2. As we saw earlier, when ℓ = 1, the magnetic quantum number m_ℓ can have values of -1, 0, +1. Starting with n = 2 and ℓ = 1, we therefore have three 2p orbitals: $3p_x$, $3p_y$, $3p_z$ (figure 13.13).

The p orbitals are nonspherical; the orbitals place most of the electron density in two «lobes» along one of the X-, Y-, or Z-axes on either side of the nucleus. These three p orbitals are identical in size, shape and energy; they differ from one another only in orientation.

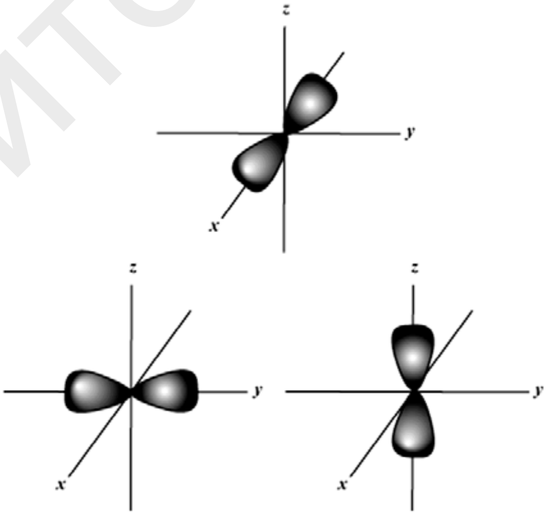


Figure 13.13 — The contour diagram for p orbitals

d Orbitals and Other Higher-Energy Orbitals

When n = 2, there are five values of m_ℓ, which correspond to five d orbitals. The lowest value of n for a в orbital is 3. Because ℓ can never be greater than n – 1, when n = 3 and $\ell = 2$, we have five 3d orbitals ($3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$, $3d_{z^2}$), shown in figure 13.14. Of these orbitals, two lie along the X-, Y- and Z-axes and three lie between the axes. The orbitals are named for the planes in which they lie; the d_{xy} orbital lies in the xy plane, etc. The other two d orbitals place electron density directly on the X-, Y- and Z-axes. The other orbital looks quite different from the other four orbitals. Most of the electron density is directed along the Z-axes, and a small «doughnut» of electron density lies in the XY plane in the d_x^2 orbital.

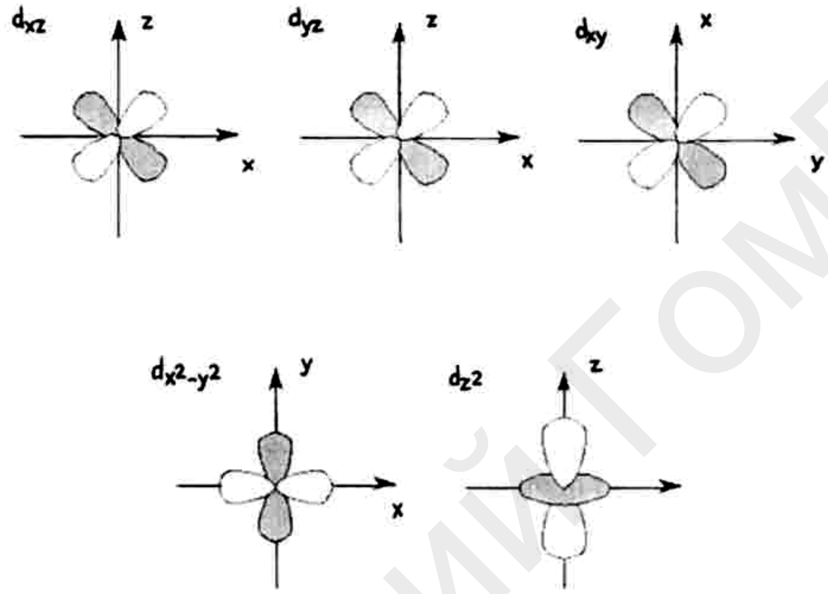


Figure 13.14 — The contour diagram for d orbitals

As we saw in Section 13.5, beyond the d orbitals are f, g, … orbitals. The f orbitals are important in accounting for the behavior of elements with atomic numbers greater than 57, although their shapes are difficult to represent.

Orbital sizes are determined mainly by the principle quantum number. Orbitals with the same value of n but different values of ℓ, m_ℓ, and s have similar sizes (but different shapes). In an atom, as n increases, the orbital size increases. As n increases, the energy of the electron increases. A more energetic electron occupies more space; therefore the orbital describing the electron must be larger.

Orbitals become smaller as the nuclear charge increases. An electron is attracted to the nucleus by electrical forces; as the size of the positive charge on the nucleus increases, so does the force on the electron. The increased force will keep the electron closer to the nucleus, so the orbital for the electron will be smaller. The size of an orbital has many important consequences that we will discuss in later chapters.

Along with the shapes and sizes of atomic orbitals, we are now ready to inquire into their **relative energies** and how these energy levels help determine the actual electronic arrangements found in atom. The energy of an electron depends not only on its principle quantum number but also on its angular momentum quantum number. The ordering of orbital energy levels is represented in figure 13.15. Orbitals that have the same energy are said to be **degenerate orbitals**.

For many-electron atoms, the 3d energy level is very close to the 4s energy level. The total energy of an atom, however, depends not only on the sum of the orbital energies but also on the energy of repulsion between the electrons in these orbitals. In turns out that the total energy of an atom is lower when the 4s subshell is filled before a 3d subshell. Figure 13.16 is a helpful diagram of the order in which atomic orbitals are filled in a many-electron atom.

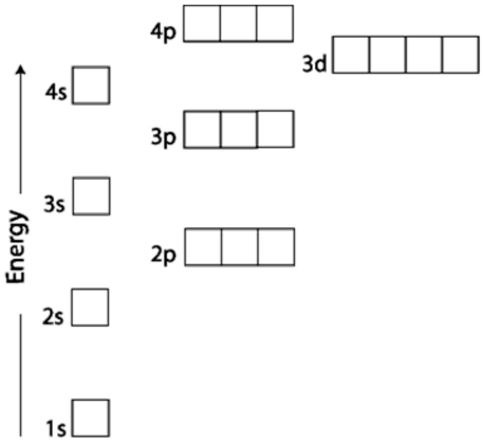


Figure 13.15 — Orbital energy level in a many-electron atom note that the energy level depends on both n and ℓ

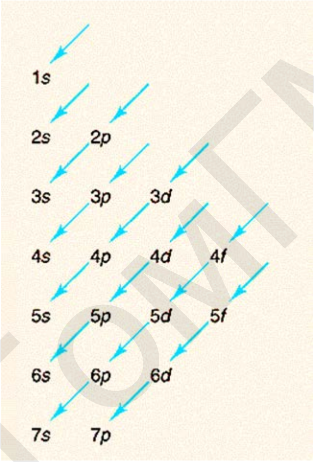


Figure 13.16 — The order in which atomic subshells are filled in a many electron atom

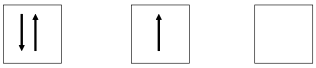
13.6. Electron configurations

Each atomic electron can be described by a set of four quantum numbers, and a description of all electrons in an atom is an **electron configuration**. There are an infinity number of acceptable sets of quantum numbers, but only one set describes an atom in its most stable form. This set is the **ground-state configuration**. The principles for determining ground-state configurations are the focus of this section.

The Pauli's Exclusion Principle. In 1925 Wolfgang Pauli postulated that **no two electrons in an atom can have the same four quantum numbers**. In other words, a given set of quantum numbers n, ℓ, m_ℓ and m_s can characterize only one electron. Any other electron in that atom must have at least one quantum number different in value. It follows directly from Pauli's exclusion principle that no more than two electrons can be present in an orbital, with $m_s=+\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

Austrian-born scientist **Wolfgang Ernst Pauli** (1900–1958) made numerous important contributions to twentieth-century theoretical physics, including explaining the Zeeman effect, first postulating the existence of the neutrino and developing what has come to be known as the Pauli exclusion principle. A cornerstone of the modern understanding of matter, the exclusion principle garnered Pauli the Nobel Prize in Physics in 1945.

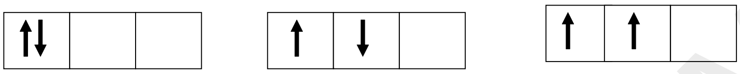
The three possible ways of placing electrons in an orbital are as follows:



(a) (b) (c)

In the diagram (a) two electrons in an orbital take opposite values of the electron spin quantum numbers. The diagram (b) represents an unpaired electron, and the diagram (c) corresponds to a vacant orbital (free of electrons).

Hund's Rule. The electron configuration of carbon is $1s^{2}2s^{2}2p^{2}$. The following are different ways for placing two electrons among three p orbitals:



(a) (b) (c)

None of the three arrangements violates the Pauli's exclusion principle, so we must determine which one will give the greatest stability. The answer is provided by Hund's rule, which states **that the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins**. The arrangement shown in (c) satisfies this condition. In both (a) and (b) the two spins cancel each other. Thus the electron configuration of carbon is $as^{2}2s^{2}2p^{2}$, and its orbital diagram is:

$1s^2$ $2s^2$ $2p^2$

Frederic Hund (1896–1997) is the German physicist whose work was mainly in quantum mechanics. He also helped to develop the molecular orbital theory which explains the nature of chemical bonding.

13.7. Physiochemical parameters of atoms

The periodic trends in electron configuration result in periodic trends in chemical and physical properties. Here, we consider a few of them: atomic radius, ionization energy, electron affinity, and electronegativity.

Atomic Radius. An atom does not have a definite size. Mathematically, the wave function of an atom extends to infinity. Therefore, we need to define it in a somewhat arbitrary manner. **Atomic Orbital Radius** is a theoretically calculated distance from the nucleus to the maximum of electron density in the outer orbital (R, nm).

Ionization Energy (I, kJ/mol) is the minimum amount of energy required to remove an electron from a gaseous atom in its ground state:

$$\text{Energy} + E \rightarrow E^{+} + \bar{e}$$

where E represents an atom of any element. This measurement gives the first ionization energy. The process can be continued to give the second, third ..,

$$\text{Energy} + E^{+} \rightarrow E^{2+} + \bar{e}$$
$$\text{Energy} + E^{2+} \rightarrow E^{3+} + \bar{e}$$

Figure 13.17 lists ionization energies for the first twenty elements versus atomic number.

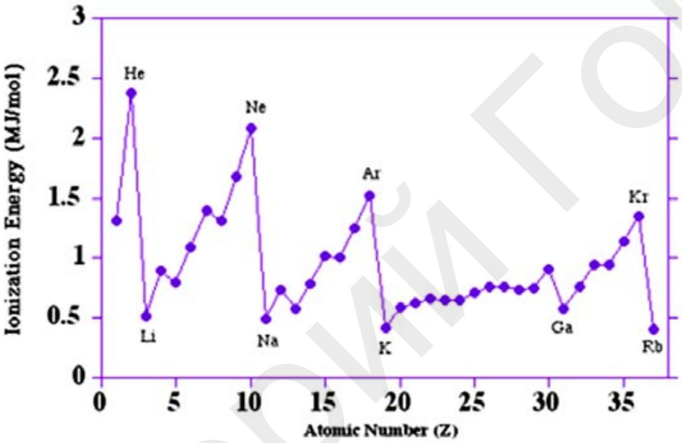


Figure 13.17 — The plot of the first ionization energies versus atomic number for the first 37elements

The effective nuclear charge increases across a period from left to right, and so the ionization energy also increases because the outermost electron is held more tightly. Down a group, the outermost electron is placed in successive outer shells, where it is effectively shielded by the inner electrons and can be removed more easily than the element above it.

Electron Affinity (F, kJ/mol) is defined as the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion:

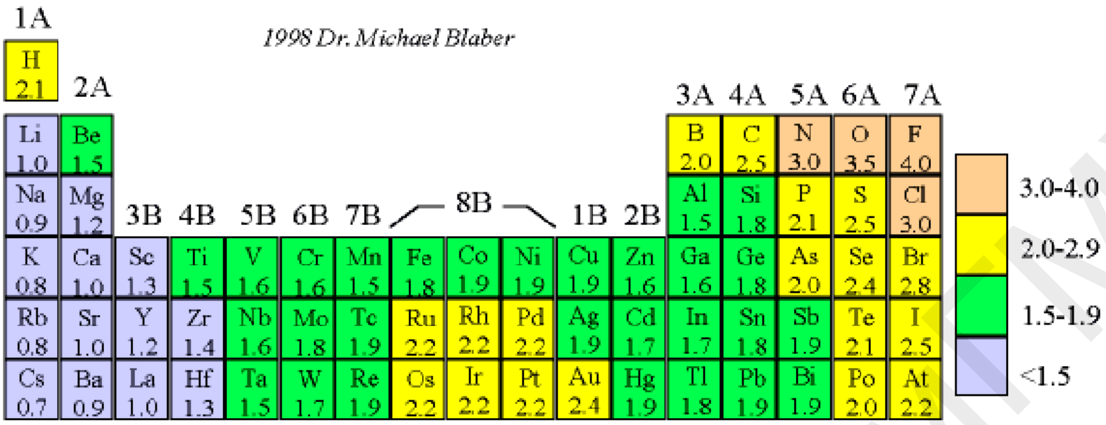
$$E + \bar{e} \rightarrow X^{-}$$

In contrast to ionization energies, electron affinities are difficult to measure. The more positive the electron affinity, the greater the tendency of the atom to accept an electron.

Electronegativity is the ability of an atom to attract electrons toward itself in a chemical bond. It is a parameter introduced by Linus Pauling in 1932. Electronegativity is related to electron affinity and ionization energy according to the equation:

$$(\chi) \approx ½ \times (I + F)$$

L. Pauling suggested the scale of electronegativities (figure 13.18).

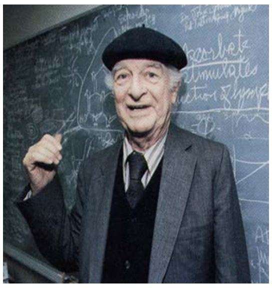


1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A
H 2.1																
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2

Figure 13.18 — Electronegativity scale of the elements

Metals generally have low electronegativity. For example, metals in the s block have $\chi \leq 1$, except for magnesium ($\chi = 1.3$) and beryllium ($\chi = 1.6$). Non-metals have high electronegativities, which range from phosphorus and hydrogen ($\chi = 2.1$) to fluorine ($\chi = 4.1$) which is the most electronegative atom. The general trends in changing electronegativity of atoms are:

- electronegativity increases from left to right along a period;
- for the representative elements (s and p block) the electronegativity decreases as you go down a group;
- the transition metal group (d block) is not as predictable as far as electronegativity.



Linus Pauling (1901–1994) is the only sole recipient of two Nobel Prizes, including the Nobel Peace Prize in 1962. He has influenced many different areas of science and politics, and has been mentioned as one of the twenty greatest scientists of all time.

13.8. Problems discussion questions

1. Explain what is meant by the statement that matter and radiation have a «dual nature».

2. What is the physical significance of the way function?

3. Define atomic orbital. Describe the characteristics of an *s* orbital, a *p* orbital, and a *d* orbital?

4. Describe the four quantum numbers used to characterize an electron an electron in an atom.

5. Define the following terms: electron configuration, the Pauli's exclusion principle, Hund's rule.

6. Explain why the ground-state electron configurations for Cr and Cu are different from what we might expect.

NUMERICAL EXERCISES

ISOTOPES

7. What are the names and the compositions of the nuclei of the three isotopes of hydrogen? What do these nuclei have in common? In what specific way do they differ? In atoms having these nuclei, what else is the same?

8. Which of the following are isotopes? (Use the hypothetical symbols for your answer).

M has 12 protons and 13 neutrons
Q has 13 protons and 13 neutrons
X has 12 protons and 12 neutrons
Я has 13 protons and 12 neutrons

9. Write the atomic symbol for the isotopes of oxygen (atomic number 8) that has a mass number of 18.

10. Write the atomic symbol for the isotopes of cobalt (atomic number 27) that has 33 neutrons. (This is a radioactive isotope used in cancer treatment).

11. Carbon, atomic number 6, has three isotopes that are found in nature. The most abundant (98.89 %) has a mass number of 12. The isotope with a mass number of 13 makes up 1.11 % of naturally-occurring carbon. The third isotope — obviously present in the merest trace, makes possible the dating of ancient artifacts.

(a) What is the same about these isotopes?
(b) In what specific feature of atomic structure do they differ?

ELECTRONIC CONFIGURATION AND ATOMIC PROPERTIES

12. An electron is in a certain atom is in the n = 2 quantum level. List the possible values of ℓ and m_ℓ that it can have.

13. An electron is in a certain atom is in the n = 3 quantum level. List the possible values of ℓ and m_ℓ that it can have.

14. Give the values of the quantum numbers associated with the following orbitals:

(a) 2p, (b) 3s, (c) 5d.

Write the ground-state electron configurations for the following elements:

(a) B, (b) Ne, (c) P, (d) Mn, (e) Cd, (f) Pb, (g) I.

15. Which of the following species has the most unpaired electrons? S^+, S, or S^-. Explain how you arrive at your answer.

17. Write the ground-state electron configurations of the following ions, which play important roles in biochemical processes in our bodies:

(a) Na^+, (b) Mg^{2+}, (c) Ca^{2+}, (d) Fe^{2+}, (e) Cu^{2+}, (f) Zn^{2+}, (g) Cl^-.

18. Explain, in terms of their electron configurations, why Fe^{2+} is more easily oxidized to Fe^{3+} than Mn^{2+} is to Mn^{3+}.

19. The electron configuration of a neutral atom is $1s^22s^22p^63s^2$. Write a complete set of quantum numbers for each of the electrons. Name the element.

20. Draw orbital diagrams for atoms with the following electron configurations:

(a) $1s^22s^22p^5$, (b) $1s^22s^22p^63s^23p^3$, (c) $1s^22s^22p^63s^23p^64s^23d^7$.

21. The electron configurations described in this chapter all refer to atoms in their ground states. An atom may absorb a quantum of energy and promote one of its electrons to a higher-energy orbital. When it happens, we say that the atom is in an exited state. The electron configurations of some exited atoms are given. Identify these atoms and write their ground-state configurations:

(a) $1s^22s^22p^63d^1$, (b) $1s^22s^1$, (c) $1s^22s^22p^64s^1$.

22. In 1996, physicists created an antiatom of hydrogen. In such an atom, which is the antimatter equivalent of an ordinary atom, the electrical charges of all the component particles are reversed. Thus, the nucleus of an antiatom is made of an antiproton, which has the same mass as a proton but bears a negative charge, whereas the electron is replaced by an antielectron (also called positron) with the same mass as an electron but bearing a positive charge. Would you expect the energy levels and atomic orbitals of an antihydrogen atom to be different from those of a hydrogen atom? What would happen if an antiatom of hydrogen collided with a hydrogen atom?

CHAPTER 14
THE CHEMICAL BOND

I believe the chemical bond is not so
simple as some people seem to think.
Robert S. Mulliken

After reading this chapter, you should be able to:

- define the types of chemical bonds and the types of interactions between molecules;
- define the covalent bond, its strength and polarity. Give the examples of covalent compounds;
- be able to discuss the valence bond and molecular orbitals theories;
- discuss the theory of hybridization and configurations of molecules. Define bond polarity;
- define ionic bond and discuss the structure of crystal lattices and physical properties of ionic compounds;
- discuss the hydrogen bonding and give the examples of inter- and intramolecular interactions of molecules and their functional groups.

The theory of the chemical bond is the central problem of modern chemistry. Without the knowledge of the nature of the interaction between the atoms in matter it is impossible to understand the reason for the variety of chemical compounds or the mechanism of their formation, or their composition, structure, and reactive properties. Using what we have learned in Chapter 13 about quantum mechanics and the electronic structure of atoms, we now begin our study of molecules. How can we explain the fact that two hydrogen atoms will combine to form a stable H_2 molecule, but two helium atoms will not form a stable He_2 molecule? Why are the water molecule bent and the carbon dioxide molecule linear? The answers to all these questions and many more, must come from quantum mechanics.

This chapter will survey the important theories of chemical bonding, and some molecular properties.

14.1. The nature of chemical bond

Chemical bond is the result of interaction between atoms which gives stable polyatomic systems. Bonds form because the resulting molecule is more stable than the separated atoms. Thus the main requirement for the chemical bond formation is the lowering of the total energy of a polyatomic system in comparison with the energy of isolated atoms.

Atoms achieve maximum stability when their electrons occupy the atomic orbitals of the lowest possible energies, and ions achieve maximum stability when they cluster in ionic solids. Molecules, on the other hand, achieve maximum stability when electrons are shared between nuclei. So a molecule can be defined as a stable electro neutral system composed of electrons and nuclei.

Chemical bond is electrical in origin. All charged species are subject to Coulomb's law:

$$\mathbf{E}_{\mathbf{coulomb}} = \mathbf{k}\frac{\mathbf{q}_1 \times \mathbf{q}_2}{\mathbf{r}}, \tag{14.1}$$

where q_1 and q_2 are the magnitudes of the charges, and r is the distance between them.

Equation 14.1 describes the energy of one pair of charges, such as one electron attracted to one nucleus, but molecules contain two or more nuclei and two or more electrons. To obtain the total coulombic energy of a molecule, Equation 14.1 must be applied to every possible pair of charged species. These pairwise interactions are of three types. First, electrons and nuclei are oppositely charged, so electron-nucleus interactions generate negative energies and stabilize a molecule. Second, electrons repel each other, so electron-electron interactions give positive energies and destabilize a molecule. Third, nuclei repel each other, so nucleus-nucleus interactions also destabilize a molecule.

Let's consider the change in potential energy of a system composed of the two hydrogen atoms when they are coming nearer. As two hydrogen atoms come together, the molecule is stabilized by attractive forces between the nuclei and the electrons. The amount of stabilization varies with the separation between the nuclei, as shown in figure 14.1.

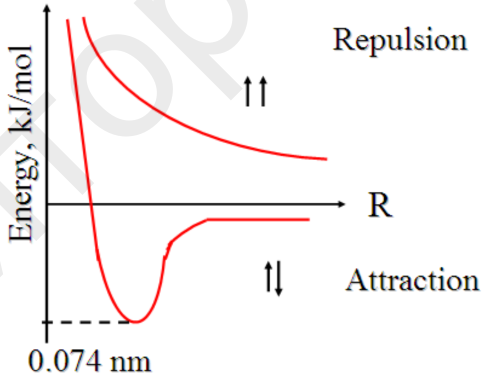
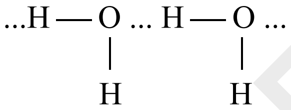


Figure 14.1 — Potential-energy curves for the H_2 molecule

At distances greater than 0.3 nm, there is almost no interaction between the atoms, and the energy of the two atoms is just the sum of their atomic energies. At closer distances the attraction between the electrons and the nuclei increases, and energy is released. Moving the nuclei closer together generates greater stability until they are 0.074 nm apart. At distances closer than 0.074 nm, however, the nucleus-nucleus repulsion increases more rapidly than the electron-nucleus attraction. Thus at a separation distance of 0.074 nm, the molecule is at the bottom of an «energy well», where it is most stable. The atoms are combined in a molecule, sharing two electrons in a covalent bond. Keep in mind that those two hydrogen atoms are joined together when atoms have opposite spins of their electrons. When atoms exhibit the parallel spin of electrons, the chemical bond doesn’t form.

Figure 14.1 shows two characteristic features of chemical bonds. The separation distance where the molecule is most stable is known as the **bond length**, and the amount of stability at this separation distance is known as the **bond energy** or strength of the bond. **Bond Energy** (E, kJ/mol) is also defined as the amount of energy required to break a particular bond in a mole of molecules in a gaseous state. Bond energies of different types of bonding are represented in the table 14.1.

Table 14.1 — The Bond Energy of different types of Chemical Bonding

Chemical Bond	Examples	Bond Energy, kJ/mol
Covalent	H—H H—Cl	200–800
Ionic	$Na^+ Cl^-$	40–400
Hydrogen bond	 $\ldots H-\underset{\substack{\vert \\ H}}{O}\ldots H-\underset{\substack{\vert \\ H}}{O}\ldots$	4–40
Ion — Dipole Forces	$Na^+(H_2O)_n$	5–60
Dipole — Dipole Forces	$SO_2 \ldots SO_2$	0.5–15
Dispersion Forces	He…He	4–40

14.2. Covalent bond

A Covalent Bond is a bond formed by the sharing of one, two or three pairs of electrons by two atoms. The bonded atoms will experience some level of increased stability as a result of the sharing process. The shared electrons will reside primarily between the two bonded nuclei. This will produce an electrostatic force of attraction between the nuclei and the shared electron orbital. This force holds the bonded system together.

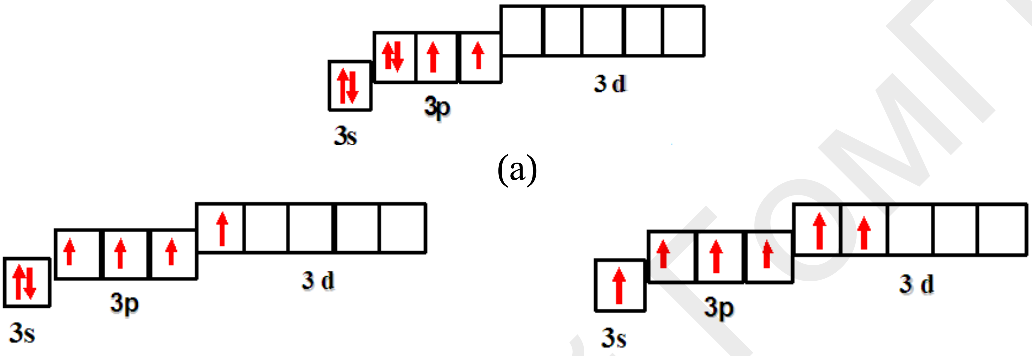
Covalent bond is the strongest chemical bond which is wide spread in nature. Practically all bonds in organic compounds are covalent. There are two quantum mechanical theories to describe the covalent bond: Valence bond (VB) theory and Molecular orbital (MO) theory.

Valence Bond Theory of Covalent Bond

The valence bond theory was the first quantum mechanical theory of bonding to be developed. In 1916, G. N. Lewis proposed that a chemical bond is formed by the interaction of two shared bonding electrons. In 1927 the Heitler-London theory was formulated which for the first time enabled the calculation of bonding properties of the hydrogen molecule H_2 based on quantum mechanical considerations. Later, L. Pauling used the pair bonding ideas of Lewis together with Heitler-London theory to develop two other key concepts in VB theory: resonance (1928) and orbital hybridization (1930). **VB theory assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms**.

The underlying principle of the VB theory is that only valence electrons take part in covalent bond formation. **Valence electrons** are the outer electrons of an atom which are involved in chemical bonding. The number of covalent bonds that an atom can have in a molecule is called the covalence number. **Covalence number** of an atom can be predicted as a number of unpaired electrons in its ground and energetically excited states.

Let us consider the possible covalence numbers of sulfur atom at its ground and exited states. The electron configuration of S is $1s^22s^22p^63s^23p^4$. The orbital diagrams for S atoms are represented in figure 14.2.



(a)

(b) (c)

Figure 14.2 — Orbital diagrams for sulfur atom (a) at its ground state, (b) excited state -1, (c) excited state -2

There are two unpaired electrons at the ground state of S thus it exhibits a covalent number 2. When an atom adsorbs some amount of energy one electron is promoted from the 3p subshell to the 3d subshell, thus the exited state -1 is achieved. This state corresponds to covalent number 4 because there are four unpaired electrons in outer shells of an atom. The extra amount of energy absorbed by an atom promotes one electron from the 3s subshell to the 3d subshell. At excited state -2 the covalent number of sulfur is six.

The electron pairs shared by two atoms can be arranged either by **coupling** or by **donor-acceptor mechanisms**. Coupling mechanism is the pairing of unpaired electrons of two different atoms. For example, the hydrogen molecule H_2 is generated when unpaired 1s electrons in two hydrogen atoms join together to form an electron pair shared by two atoms:

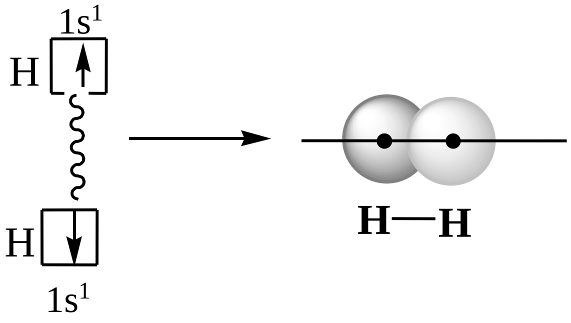
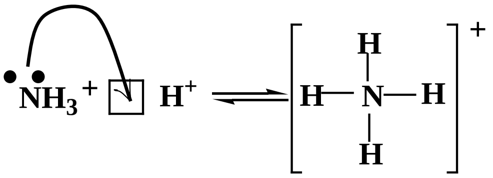


Figure 14.3 — The coupling mechanism of hydrogen molecule formation

Donor-acceptor mechanism is operating when one atom donates a lone electron pair to the vacant orbital of another atom. The atom donating an electron pair for the formation of a bond is called **a donor**, while the one providing a vacant orbital is called an **acceptor.** A classical example is the formation of an ammonium cation NH_4^+. Nitrogen atom donates its lone electron pair to the vacant orbital of hydrogen cation H^+:



$$\ddot{N}H_3 + \square\, H^+ \rightleftharpoons \left[H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}-H \right]^+$$

The bond formed by the donor-acceptor mechanism (represented by an arrow directed from atom-donor to atom acceptor) does not differ in its characteristics from the other covalent bonds of nitrogen and hydrogen formed in the conventional way.

Bond order (n) equals to the number of electron pairs shared by two atoms. An increase in the multiplicity of a bond reduces the internuclear distance and strengthens the bond between atoms. Characteristics of single and multiple bonds are given in table 14.2. Inspection of table 14.2 reveals that the energy of a double bond $C = C$ (or a triple one $C \equiv C$) is less than the double (or triple) energy of a single bond $C – C$.

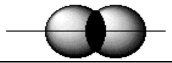
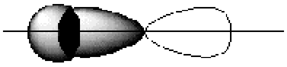
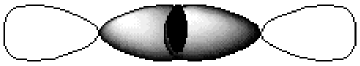
Table 14.2 — Characteristics of Single and Multiple Bonds

Molecule	Bond	Bond length, nm	Bond energy, kJ/mol
C_2H_6	$C – C$	0.154	348
C_2H_4	$C = C$	0.135	635
C_2H_2	$C \equiv C$	0.120	830

The valence-bond approach considers the overlap of the atomic orbitals (AO) of the participation atoms to form a chemical bond. Due to the overlapping, electrons are localized in the bond region. The overlapping AO’s can be of different types. There are two main types of atomic orbitals’ overlap:

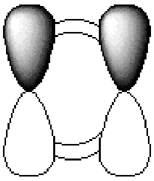
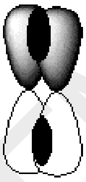
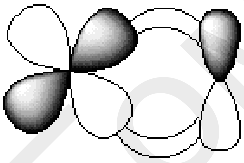
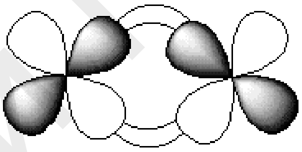
(a) **end-on overlap** of orbitals directed towards each other. As illustrated in Table 14.3, this type of overlap gives high electron density distributed symmetrically along the axis. A bond of this type is called a sigma (σ) bond. **Sigma bonds** have high electron density distributed symmetrically along the bond axis.

Table 14.3 — End-on Overlap of Atomic Orbitals. The Formation of σ-Bonds

Orbitals used in bond formation	**σ-Bond, showing the head on overlap of atomic orbitals**
s-orbital — s-orbital	
s-orbital — p-orbital	
p-orbital — p-orbital	

(b) **side-by-side overlap** of atomic orbitals is above and below the bond internuclear axis. Side-by-side overlap results in **π-bond** formation (table 14.4).

Table 14.4 — Side-by-side Overlap of Atomic Orbitals. The Formation of π-Bonds

Orbitals used in bond formation	**π-Bond, showing the side-ways overlap of atomic orbitals**
p_y-orbital — p_y-orbital	  overlap also illustrated like so
$3d_{xy}$-orbital — p_y-orbital	
$3d_{xy}$-orbital — $3d_{xy}$-orbital	

The greater the degree of overlap of the atomic orbitals, the greater will be the degree of sharing and the stronger will be the covalent bond between them. This statement explains why σ-bonds are stronger than π-bonds.

The atomic orbitals can be the original atomic orbitals of the atoms, but often the geometry of these orbitals is such that effective overlap cannot occur in the known geometry of the molecule. Under these circumstances, the atomic orbitals on an atom can reconfigure themselves into a different configuration, and the reconfigured orbitals are said to be hybridized. **Hybridization** is the process of mixing the atomic orbitals in an atom to generate a set of new atomic orbitals with different spatial distributions. Hybridization requires an input of energy; however, the system more than recovers this energy during bond formation.

Figure 14.4 — The Centaur is an image of a hybrid orbital

It’s a race of monsters in Greek mythology, hybrid animal having the head, arms and torso of a man united to the body and legs of a horse.

Hybridized orbitals are assumed to be mixtures of these atomic orbitals, superimposed on each other in various proportions. For example, the mixing of s- and p-orbitals resulting in the formation of sp-hybrid orbitals is represented in figure 14.5.

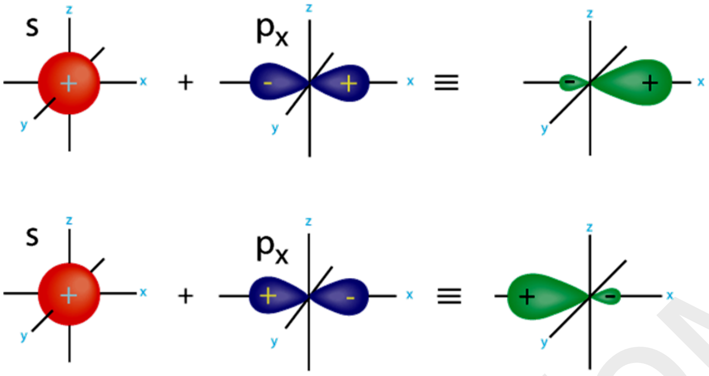


Figure 14.5 — The formation of sp-hybrid orbitals

The hybridization of atomic orbitals approach is most easily used when a molecule consists of some arrangement about a single atom, i.e. where a single atom is at the center of symmetry of the molecule. Such an atom is defined as a central in a molecule; it exhibits the highest covalence number.

The primary reason for qualitative use of this approach is because it gives information on the molecular geometry. Hybridized orbitals are very useful in the explanation of the shape of molecules. A type of central atom hybridization determines configuration of molecules. **Configuration** is a stereo arrangement of atoms in a molecule. Table 14.5 shows the sp, sp^2, sp^3, sp^{3}d and sp^{3}d^2 hybridizations and the shapes of the hybrid orbitals.

It is important to note that for molecules made up from carbon, nitrogen and oxygen (and to a lesser extent, sulfur and phosphorus) the hybridization theory makes the description much easier. The hybridization theory finds its use mainly in organic chemistry, and mostly concerns C, N and O (and to a lesser extent P and S).

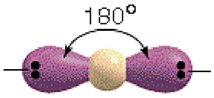
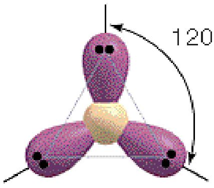
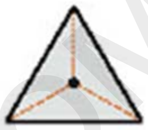
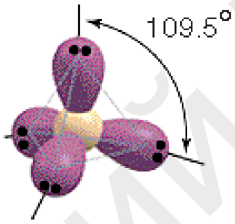
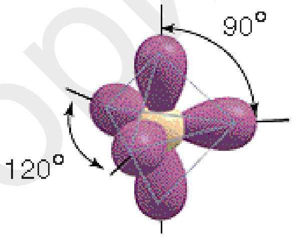
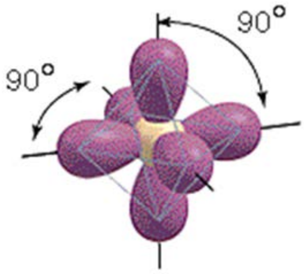
Covalent bond can be of the two types: **nonpolar** and **polar**. A general rule for predicting the type of bond based upon electronegativity differences. If the electronegativities are equal (i.e. if the electronegativity difference is 0), the bond is non-polar, but if the difference in electronegativities between the two atoms is greater than 0, but less than 2.0, the bond is polar. When the difference in electronegativities between the two atoms is 2.0, or greater, the bond is ionic.

Nonpolar covalent bonds link atoms of the same chemical element, for example, H-H, O=O, N ≡ N. In such molecules the electron density is distributed symmetrically between the nuclei.

Polar covalent bonds link atoms of different elements: H-Cl, H-O-H, and C≡O. When covalent bonds are formed between atoms of different electronegativities the result is that the shared electrons skew more toward one atom than the other.

The resulting molecule is a dipole: the higher electronegative atom in the bond gains a **partial negative charge (-δ)** while the less electronegative atom becomes **partially positive (+δ).**

Table 14.5 — Important Hybrid Orbitals and their Shapes

Pure atomic orbitals of the central atom	**Hybridi-zation of the central atom**	**Shape of hybrid orbitals**	**Molecular Geometry**	**Examples**
s, p	***sp***		**Linear**	**$BeCl_2$**
s, p, p	***sp^2***		**Trigonal Planar** 	**BCl_3**
s, p, p, p	***sp^3***		**Tetrahedral** 	**CH_4**
s,p,p,p,d	***dsp^3***		**Trigonal Bipyramidal** 	**PCl_5**
s,p,p,p,d,d	***d^2sp^3***		**Octahedral** 	**SF6**

The measure of the overall polarity of a covalent bond is called the **dipole moment (μ):**

$$\mu = \ell \times \delta, \tag{14.2}$$

where ℓ is a distance between negative and positive poles in a molecule;

δ is a partial charge of atoms in a molecule.

Dipole moment is measured in the **debye** (D) in honor of Debye, who pioneered the studying of molecules' polarity.

As the value of the dipole moment increases, so does the polarity of the molecule. Thus a molecule that possesses a dipole moment is called a polar molecule; a molecule that does not possess a dipole molecule is called a nonpolar molecule. For example, in the HF molecule, the shared electron pair is attracted toward the more electronegative fluorine atom (electronegativity 4.1), which causes a partial negative charge to form in it, and a partial positive charge to form on the hydrogen atom (electronegativity 2.1):

$$\overset{\delta+}{\mathbf{H}} - \overset{\delta-}{\mathbf{F}}$$

Table 14.6 lists the dipole moments and partial electric charges of atoms in several polar diatomic molecules.

Table 14.6 — The magnitudes of partial electric charges of atoms in molecules and their dipole moments

Molecule	**μ, D**	**Partial electric charges**
HF	5.82	± 0.77
HCl	1.08	± 0.18
CO	0.11	± 0.02

The dipole moment of a molecule containing three or more atoms depends on both polarity and molecular geometry. For example, even if polar bonds are present, the molecule itself may not have a dipole moment.

Symmetric (linear) molecules are usually nonpolar. Let us consider the carbon dioxide (CO_2) molecule (figure 14.6). The arrows show the shift of electron density from the less electronegative carbon atom to the more electronegative oxygen atom. We can say that each arrow represents a dipole moment of a bond. The dipole of the entire molecule is made up of two bond moments. It is clear that the two bond moments on CO_2 are equal in magnitude. Since they point in opposite directions in a linear CO_2 molecule, the sum or resultant dipole moment would be zero. Thus the CO_2 molecule is nonpolar that was confirmed through the experimental measurements.

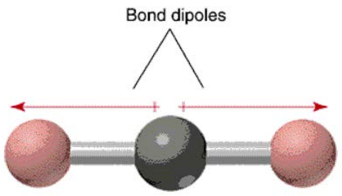


Figure 14.6 — Carbon dioxide molecule is nonpolar because it is linear.

Asymmetric (bent) molecules are polar if there are polar bonds in the structure. Let us consider the H_2O molecule (figure 14.7). The arrows represent the bond dipoles that are directed toward oxygen since its electronegativity is greater than that of hydrogen. Water molecule is polar because its overall dipole moment is greater than zero.

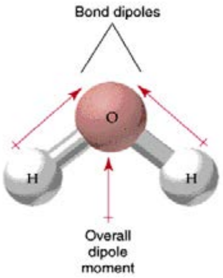


Figure 14.7 — Water molecule is polar because it exhibits the bent conformation

Molecular Orbital Theory of Covalent Bond

The second theory of chemical bonding, molecular orbital (MO) theory was developed, in the years after valence bond theory (1927) had been established, primarily through the efforts of Friedrich Hund, Robert Mulliken, John C. Slater, and John Lennard-Jones. MO theory assumes that in atoms, electrons occupy atomic orbitals, but in molecules they occupy similar **molecular orbitals** which surround the molecule. Molecular orbitals arise from the linear combination of the atomic orbitals. In this LCAO-MO (linear combination of atomic orbitals-molecular orbitals) model, the wavefunctions for the molecular orbitals are given by:

$$\Psi\ (\text{bonding}) = \Psi_A + \Psi_B \qquad (14.3)$$

$$\Psi\ (\text{antibonding}) = \Psi_A + \Psi_B \qquad (14.4)$$

where the plus sign denotes the **bonding molecular orbital** and the minus sign denotes the **antibonding molecular orbital**. In other words, bonding MO is the result of AO's wavefunctions summation. Bonding MO's energy is lower than that of its constituent atomic orbitals. Antibonding MO is the result of AO's wave functions subtraction. MO's energy is higher than that of its constituent atomic orbitals. The relative energy levels of s-atomic orbitals and corresponding sigma bonding (σ) and antibonding (σ^*) molecular orbitals are given in figure 14.8.

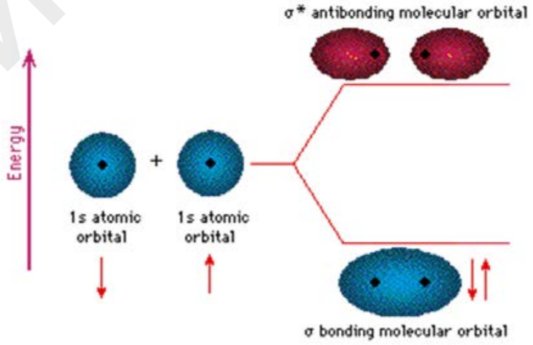


Figure 14.8 — The formation of bonding and antibonding molecular orbitals as the result the 1s atomic orbitals linear combination

The linear combination of p atomic orbitals suggests the two types of molecular orbitals. The linear overlap of the p_x orbitals gives rise to a sigma bonding and antibonding molecular orbitals. Recombination of p_y and p_z atomic orbitals gives the π MO (figure 14.9).

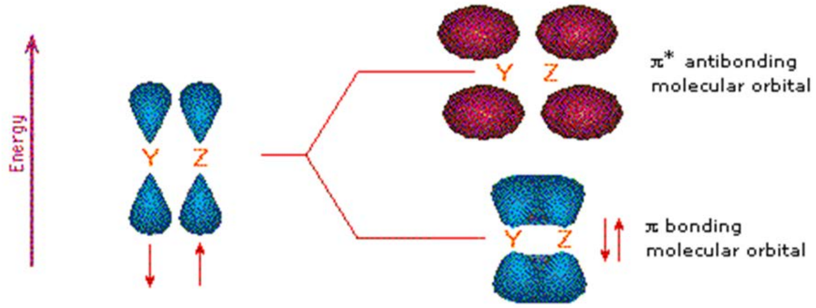


Figure 14.9 — Molecular π orbitals formation from two p-orbitals

In molecules each electron has a corresponding molecular orbital (MO) as each electron in an atom has a corresponding atomic orbital (AO). The electron configuration of molecules, like that of atoms, must satisfy both the Pauli exclusion principle and Hund's rule.

MO theory is applied to predict magnetic properties of molecules. **Paramagnetic substances** contain one or more unpaired electrons and are attracted by a magnet. **Diamagnetic substances** contain only paired electrons and are slightly repelled by a magnet.

The stability of a diatomic molecule can be estimated by calculating the number of bonds joining the atoms, or the **bond order (n),** given by

$$\mathbf{n = \frac{N - N'}{2}}, \tag{14.5}$$

where N is a number of electrons in the bonding MO; N' is a number of electrons in the antibonding MO.

Note that the bond order can be a fraction, but a bond order of 0 (or a negative value) means the bond has no stability and the molecule cannot exist. Bond order can be used only qualitatively for the purpose of comparison.

We shall now apply the MO theory to several diatomic molecules, paying particular attention to their ground-state electron configurations, stability and magnetic properties. **Molecular orbital energy-level diagrams** are applied to describe the structure of molecules and molecular ions. Each line in the diagram represents an orbital. The molecular orbital volume encompasses the whole molecule. The electrons fill the molecular orbitals of molecules like electrons fill atomic orbitals in atoms. Thus all electrons in atoms are involved in a covalent bond formation.

Hydrogen molecule H_2. The electron configuration of H is $1s^1$, in H_2 the two electrons are paired in the σ_{1s} and σ_{1s}^* is vacant. The molecular orbital energy-level diagram for hydrogen molecule is given in figure 14.10.

This molecule is diamagnetic because it doesn't contain unpaired electrons in MO's. Its bond order is one:

$$\mathbf{n = \frac{2 - 0}{2} = 1}$$

MO theory gives explanation for existence of molecular ions H_2^+ and H_2^-. Their molecular orbital energy-level diagrams are represented in figure 14.11 (a and b).

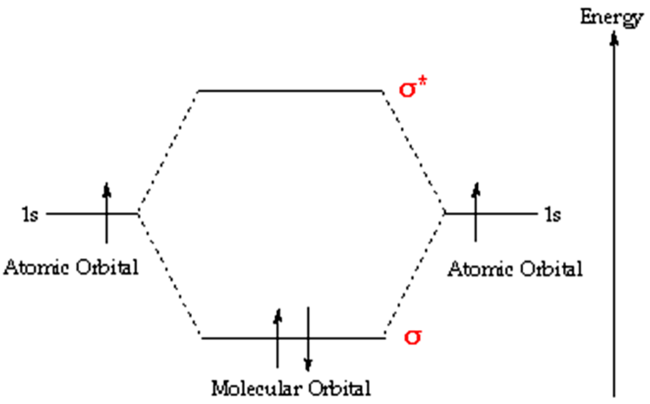
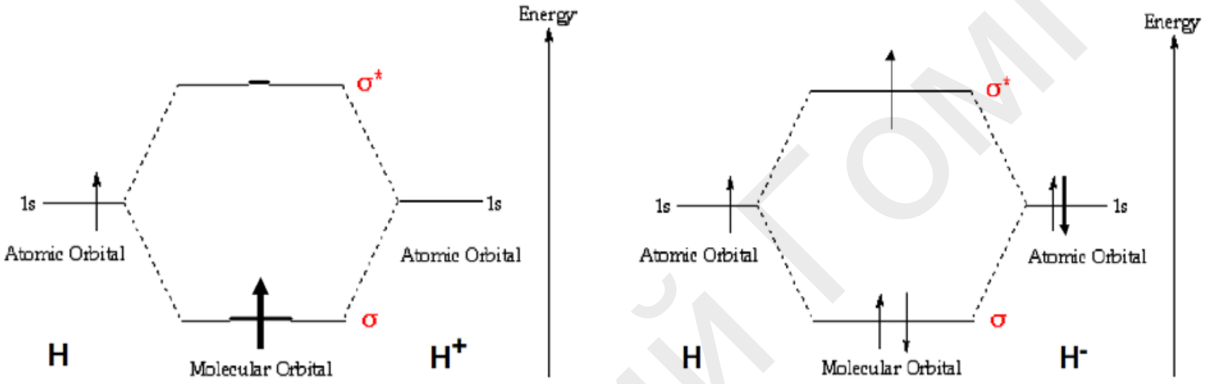


Figure 14.10 — Molecular orbital energy-level diagram for H_2 molecule



(a) **(b)**

Figure 14.11 — Molecular orbital energy-level diagrams for H_2^+cation (a) and H_2^- anion

We can assume the H_2^+cation as a combination of hydrogen atom and hydrogen cation H^+ (electron configuration $1s^0$). Thus the only one 1s electron occupies the σ_{1s} and σ_{1s}^* is vacant. The cation is paramagnetic and has bond order of ½:

$$\mathbf{n = \frac{1-0}{2} = 1/2}$$

The formation of H_2^- anion can be represented as a recombination of hydrogen atom and hydride anion H^- (electron configuration $1s^2$). Thus the two 1s electrons are paired in the σ_{1s} and an unpaired electron occupies σ_{1s}^*. The anion is paramagnetic and has bond order of ½:

$$\mathbf{n = \frac{2-1}{2} = 1/2}$$

Nitrogen molecule N_2. The electron configuration of N is $1s^22s^22p^3$. As with 1s atomic orbitals, their linear combination gives the two MO: σ_{1s} and σ_{1s}^*. The combination of $2p_s$ atomic orbitals also gives rise the two MO: σ_{2s} and σ_{2s}^*. The combination of p_x, p_y and p_z orbitals results in formation of the six MO: σ_{px} and σ_{2px}^*, π_{py} and $\pi_{py}*$, π_{pz} and $\pi_{pz}*$. According to the spectroscopic data, the molecular orbitals of diatomic molecules are arranged by energy level in the following order:

$$\sigma_{1s} < \sigma_{1s}^{*} < \sigma_{2s} < \sigma_{2s}^{*} < \sigma_{2px} < \sigma_{2px}^{*} < \pi_{2py} = \pi_{2pz} < \pi_{2py}^{*} = \pi_{2pz}^{*} < \sigma_{2px}^{*}.$$

Based on Figure 14.12, the electron configuration for N_2 is

$$(\sigma_{1s})^2(\sigma_{1s}^{*})^2(\sigma_{2s})^2(\sigma_{2s}^{*})^2(\sigma_{2p})^2(\sigma_{x})^2(\pi_{y})^2(\pi_{z}^{*})^1(\pi_{z}^{*})^1$$

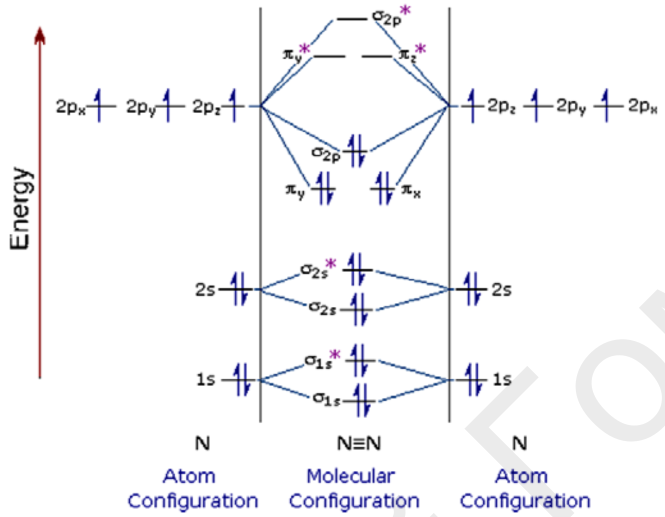


Figure 14.12 — Molecular orbital energy diagrams for N_2

The electron configuration of nitrogen molecule is responsible for magnetic properties (N_2 is a diamagnetic molecule) and its bond order of 3 (a triple bond).

Fluorine molecule F_2. The electron configuration of F is $1s^22s^22p^5$, thus there are 18 electrons in F_2 molecule. The set of molecular orbitals in F_2 is the same as in the N_2. Based on figure 14.13, the electron configuration for F_2 is:

$$(\sigma_{1s})^2(\sigma_{1s}^{*})^2(\sigma_{2s})^2(\sigma_{2s}^{*})^2(\sigma_{2p})^2(\sigma_{x})^2(\pi_{y})^2(\pi_{z}^{*})^2(\pi_{z}^{*})^2$$

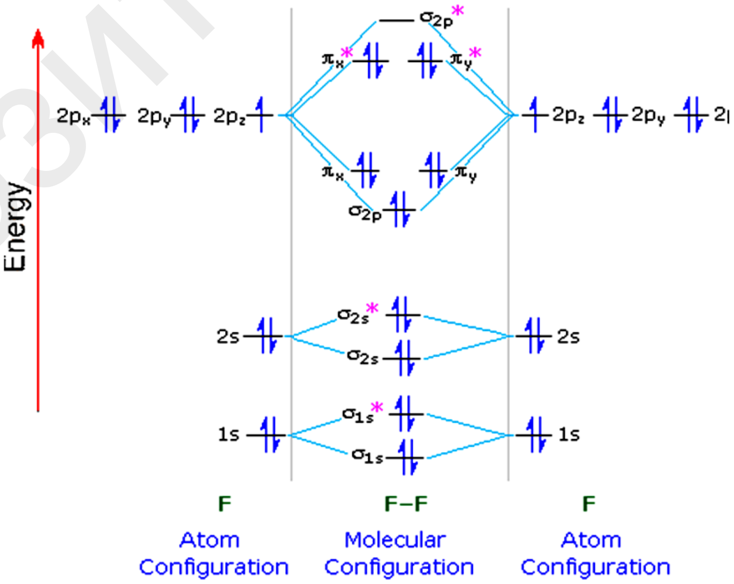


Figure 14.13 — Molecular orbital energy-level diagram for F_2

F_2 is a diamagnetic molecule and its bond order of 1 (a single bond).

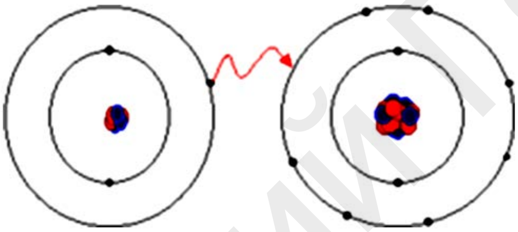
14.3. Ionic bond

An ionic bond is a type of chemical bond that involves a metal and a non-metal ion (or polyatomic ions such as ammonium) through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions.

The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond.

For example, common table salt is sodium chloride. When sodium (Na) and chlorine (Cl) are combined, the sodium atoms each lose an electron, forming a cation (Na^+), and the chlorine atoms each gain an electron to form an anion (Cl^-). These ions are then attracted to each other in a 1:1 ratio to form sodium chloride (NaCl).

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



When one electron moves from sodium to chlorine, each ion acquires the noble gas configuration. The bonding energy from the electrostatic attraction of the two oppositely-charged ions has a large enough negative value that the overall bonded state energy is lower than the unbonded state.

The removal of electrons from the atoms is endothermic and causes the ions to have a higher energy. There may also be energy changes associated with breaking of existing bonds or the addition of more than one electron to form anions. However, the attraction of the ions to each other lowers their energy.

Ionic bonding will occur only if the overall energy change for the reaction is favorable — when the bonded atoms have a lower energy than the free ones. The larger the resulting energy change, the stronger the bond. The low electronegativity of metals and high electronegativity of non-metals means that the energy change of the reaction is most favorable when metals lose electrons and non-metals gain electrons.

An ionic bond doesn’t need metal. Pure ionic bonding is not known to exist. All ionic compounds have a degree of covalent bonding. The larger is the difference in electronegativity between two atoms, the more ionic is the bond.

Dipole moments are useful for estimating the percent ionic character of a bond. If we know the bond distance in a diatomic molecule, we can calculate a dipole moment, μ_{ionic}, on the assumption that the atoms bear a full unit charge. The percent ionic character of the bond can then be calculated as:

$$\textbf{\% ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{ionic}}} \times 100\%, \qquad (14.6)$$

where μ_{exp} is the experimental dipole moment. Figure 14.14 shows a nice correlation between ionic character and the difference between the electronegativities of the two bonding atoms.

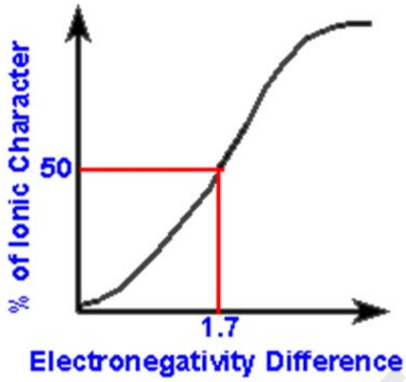


Figure 14.14 — Relation between electronegativity difference and percent ionic character in binary compounds

Table 14.7 — Common anions and cations

(a) The Cations

Common Cations			Common Cations		
common name	formula	historic name	common name	formula	historic name
Simple Cations			***Simple Cations***		
Aluminium	Al^{3+}		Magnesium	Mg^{2+}	
Barium	Ba^{2+}		Manganese(II)	Mn^{2+}	Manganous
Beryllium	Be^{2+}		Manganese(III)	Mn^{3+}	Manganic
Cesium	Cs^{+}		Manganese(IV)	Mn^{4+}	
Calcium	Ca^{2+}		Manganese(VII)	Mn^{7+}	
Chromium(II)	Cr^{2+}	Chromous	Mercury(II)	Hg^{2+}	Mercuric
Chromium(III)	Cr^{3+}	Chromic	Nickel(II)	Ni^{2+}	Nickelous
Chromium(VI)	Cr^{6+}	Chromyl	Nickel(III)	Ni^{3+}	Nickelic
Cobalt(II)	Co^{2+}	Cobaltous	Potassium	K^{+}	
Cobalt(III)	Co^{3+}	Cobaltic	Silver	Ag^{+}	
Copper(I)	Cu^{+}	Cuprous	Sodium	Na^{+}	
Copper(II)	Cu^{2+}	Cupric	Strontium	Sr^{2+}	
Copper(III)	Cu^{3+}		Tin(II)	Sn^{2+}	Stannous
Gallium	Ga^{3+}		Tin(IV)	Sn^{4+}	Stannic
Gold(I)	Au^{+}		Zinc	Zn^{2+}	
Gold(III)	Au^{3+}		***Polyatomic Cations***		
Iron(II)	Fe^{2+}	Ferrous	Ammonium	NH_4^{+}	
Iron(III)	Fe^{3+}	Ferric	Hydronium	H_3O^{+}	
Lead(II)	Pb^{2+}	Plumbous	Nitronium	NO^{2+}	
Lead(IV)	Pb^{4+}	Plumbic	Mercury(I)	Hg_2^{2+}	Mercurous
Lithium	Li^{+}				

(b) The Anions

Common Anions			**Common Anions**		
Formal Name	Formula	Alt. Name	Formal Name	Formula	Alt. Name
Simple Anions			***Oxoanions***		
Chloride	Cl^-		Iodate	IO_3^-	
Bromide	Br^-		Nitrate	NO_3^-	
Fluoride	F^-		Nitrite	NO_2^-	
Hydride	H^-		Phosphate	PO_4^{3-}	
Iodide	I^-		Hydrogen phosphate	HPO_4^{2-}	
Nitride	N^{3-}		Dihydrogen phosphate	$H_2PO_4^-$	
Oxide	O^{2-}		Permanganate	MnO_4^-	
Phosphide	P^{3-}		Phosphite	HPO_3^{2-}	
Sulfide	S^{2-}		Sulfate	SO_4^{2-}	
Oxoanions			Hydrogen sulfate	HSO_4^-	Bisulfate
Bromate	BrO_3^-		Sulfite	SO_3^{2-}	
Hypobromite	BrO^-		Hydrogen sulfite	HSO_3^-	Bisulfite
Carbonate	CO_3^{2-}	Bicarbonate	***Anions from Organic Acids***		
Hydrogen carbonate	HCO_3^-		Acetate	$C_2H_3O_2^-$	
Chlorate	ClO_3^-		Formate	HCO_2^-	
Perchlorate	ClO_4^-		Oxalate	$C_2O_4^{2-}$	
Chlorite	ClO_2^-		Hydrogen oxalate	$HC_2O_4^-$	Bioxalate
Hypochlorite	ClO^-		***Other Anions***		
Dichromate	$Cr_2O_7^{2-}$		Bisulfide	HS^-	Hydrogen sulfide

Ionic compounds in the solid state form lattice structures. In ionic crystal lattices every ion is surrounded by a limited number of counterions, which are said to be coordinated with it. The coordination number of an ion does not depend on its charge, but is determined chiefly by the ratio of the sizes of the ions of opposite signs. The two principal factors in determining the form of the lattice are the relative charges of the ions and their relative sizes. For example, at r(cation)/r(anion) = 0.41 – 0.73, octahedral coordination of the ions with a coordination number of six is observed (figure 14.15).

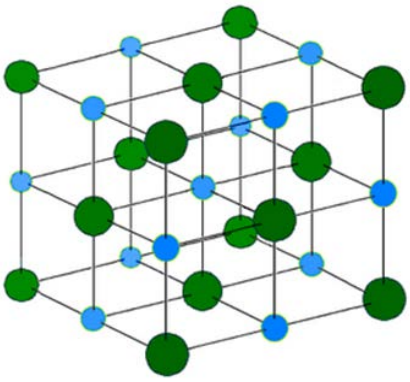


Figure 14.15 — Ionic crystal of sodium chloride

Ionic bond is responsible for the physical properties of ionic compounds that are a giant association of ions of opposite signs. Ionic compounds conduct electricity when molten or in a solution. They generally have a high melting point and tend to be soluble in water.

14.4. Hydrogen bonding

Hydrogen bond is a special type of dipole-dipole interaction between the hydrogen atom bonded to an electronegative atom (for example, O-H or N-H) and another electronegative atom. The scheme of Hydrogen bond formation is:

A – H...B,

where A and B are highly electronegative atoms: F, O, N, seldom Cl и S.

Because of its low energy hydrogen bond is represented as a dotted line. Intermolecular hydrogen bonding is responsible for association of molecules which, in its turn, effects physical properties of substances such as boiling and melting points, solubility and others.

Normally, the boiling points of a series of similar compounds containing elements in the same periodic group increase with increasing molar mass (figure 14.16). But the binary hydrogen compounds of the elements in VA-VIIA do not follow this trend. In each of these series, the lightest compounds (NH_3, H_2O, HF) have the highest boiling points, because there is extensive hydrogen bonding between molecules in these compounds.

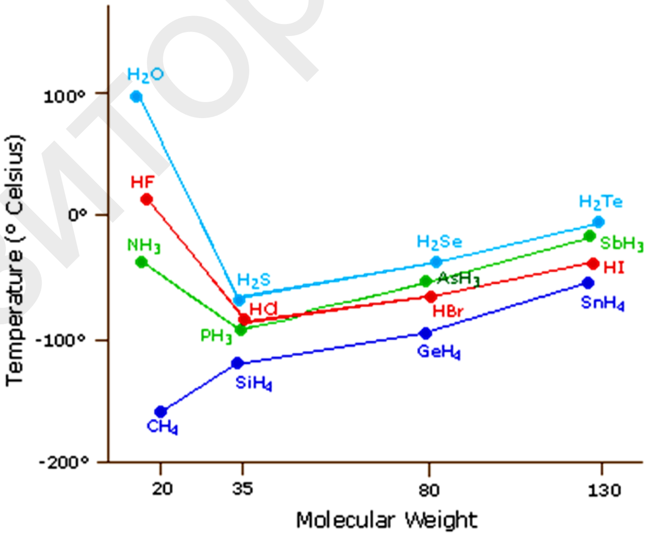


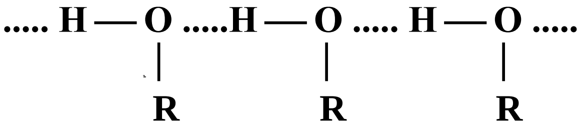
Figure 14.16 — Boiling points of the hydrogen compounds

The examples of intermolecular Hydrogen Bonding

Hydrogen fluoride. Association of HF molecule can be represented by the scheme:

.....H — F ..... H — F ..... H — F .....

Alcohols. Association of alcohols (R — OH) is represented as follows:



$$\ldots\ldots\ \mathrm{H}-\underset{\underset{\mathrm{R}}{|}}{\mathrm{O}}\ \ldots\ldots\mathrm{H}-\underset{\underset{\mathrm{R}}{|}}{\mathrm{O}}\ \ldots\ldots\ \mathrm{H}-\underset{\underset{\mathrm{R}}{|}}{\mathrm{O}}\ \ldots\ldots$$

Water. In ice one water molecule forms four hydrogen bonds thus crystallizing into three-dimension open lattice (figure 14.17).

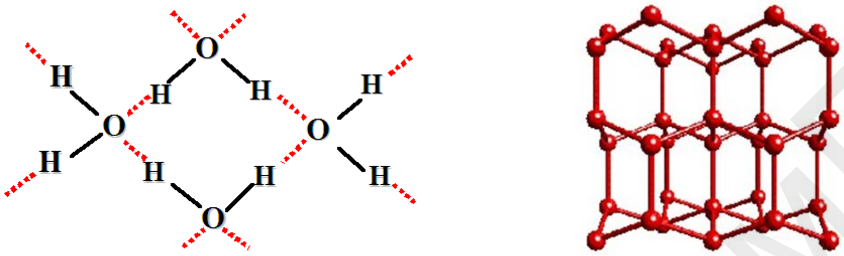
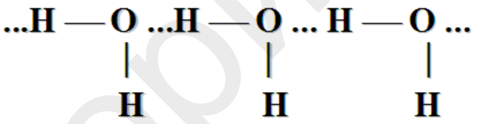


Figure 14.17 — Structure of ice

Because of its open lattice, ice has a lower density than liquid water (1.0 and 0.92 g/ml), a fact that has profound ecological significance. An ice layer formed on the surface does not sink; just as important, it acts as a thermal insulator to protect the biological environment beneath it.

Association of water molecules in liquid phase is represented by a scheme:



$$\ldots\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}\ \ldots\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}\ \ldots\ \mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{O}}\ \ldots$$

Liquid water contains both associates (clusters) and free molecules not linked by hydrogen bond (figure 14.18). Clusters are twinkling, because their half-life is ~ 10^{-10} sec. This water «super molecule» is essential to life on earth, since without it water would be a gas: however in many cases the hydrogen bonds hinder the absorption of water by living systems which need it. Placed in the electric field of these hydrogen bonds are broken and all the molecules orientated in one direction which improves the permeability of the water. (When applied to agriculture this increased permeability has been shown to give improved crop yields of up to 30 %).

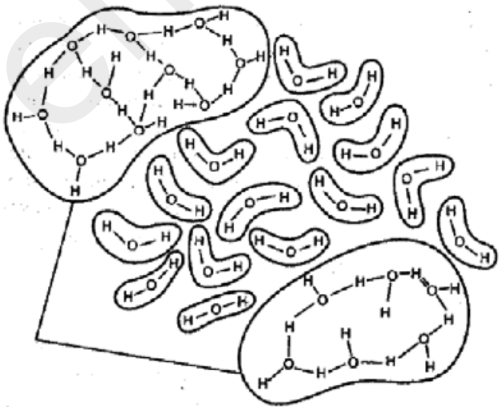
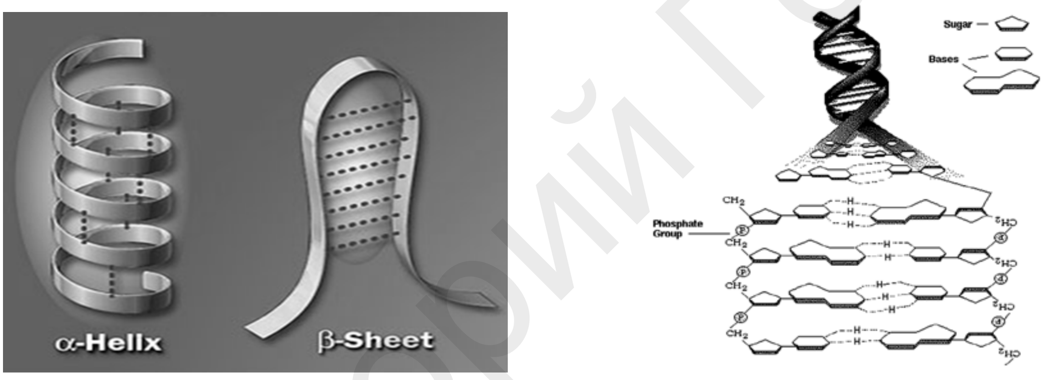


Figure 14.18 — Twinkling clusters of liquid water

A molecule can also form **intramolecular hydrogen bonds** which are responsible for stabilizing of biopolymers configurations (proteins, nucleic acids and polysaccharides). The hydrogen bond has only 5 % or so of the strength of a covalent bond. However, when many hydrogen bonds can form between two molecules (or parts of the same molecule), the resulting union can be sufficiently strong as to be quite stable.

Multiple hydrogen bonds are essential to life (figure 14.19). They fulfill important functions *in vivo*:

- hold the two strands of the DNA double helix together;
- hold polypeptides together in such secondary structures as the alpha helix and the beta conformation;
- help enzymes bind to their substrate;
- help antibodies bind to their antigen;
- help transcription factors bind to each other;
- help transcription factors bind to DNA.



(a) (b)

Figure 14.19 — Stabilization of biopolymers by hydrogen bonds:
(a) secondary structure of proteins; (b) secondary structure of DNA

14.5. Problems

DISCUSSION QUESTIONS

1. What is the polar covalent bond? Give two compounds that contain one or more polar covalent bonds.

2. Classify the following bonds as ionic, polar covalent, or covalent, and give your reasons: (a) the CC bond in H_3C-CH_3, (b) the KI bond in KI, (c) the NB bond in H_3NBCl_3, (d) the ClO bond in ClO_2, (e) the SiSi bond in $Cl_3SiSiCl_3$, (g) the CaF bond in CaF_2.

3. Arrange the following bonds in order of increasing ionic character: carbon to hydrogen, fluorine to hydrogen, bromine to hydrogen, sodium to iodine, potassium to fluorine, lithium to chlorine.

4. Use the valence bond theory to explain the bonding in Cl_2 and HCl. Show the overlap of atomic orbitals in the bond formation.

NUMERICAL EXERCISES

VALENCE-BOND THEORY AND HYBRIDIZATIION

1. The H-O-C bond angle in a molecule of methyl alcohol, CH_3OH, is about 109^o. What type of hybridization, if any, would you propose for the oxygen atom? For the carbon atom? Show the overlapping sigma orbitals in the molecule of methanol. Also show the orbitals containing the unshared (lone) electrons pairs of the oxygen atom.

2. What is the hybridization of phosphorus in PH_4^+? Predict the logical orbital and molecular geometries for a unit of PH_4^+.

3. Based solely on analogies with the compounds CH_4, NH_3, and H_2O, predict the orbital geometries and molecular shapes of SiH_4, AsH_3, and H_2Se. Taking into consideration the H-E-H bond angles (E is Si, As, or Se) in these three compounds are 109.5^o, 91.8^o, and 91.0^o, respectively answer the question.

4. What is the hybridization of atomic orbitals? Why is it impossible for an isolated atom to exist in the hybridized state?

5. How does a hybrid orbital differ from a pure atomic orbital?

6. What is the angle between the following two hybrid orbitals on the same atom? (a) sp and sp hybrid orbitals, (b) sp^2 and sp^2 hybrid orbitals, (c) sp^3 and sp^3 hybrid orbitals.

7. How would you distinguish between a sigma bond and a pi bond?

MOLECULAR ORBITAL THEORY

8. What is molecular orbital theory? How does it differ from valence bond theory?

9. Define the following terms: bonding molecular orbital, anti bonding molecular orbital, pi molecular orbital, sigma molecular orbital.

10. Explain the significance of bond order. Can bond order be used for quantitative comparisons of the strength of chemical bonds?

11. Draw a molecular orbital energy level diagram for each of the following species: He_2, HHe, He_2^+. Compare their relative stabilities in terms of bond orders.

12. Arrange the following species in order of increasing stability: Li_2, Li_2^+, Li_2^-. Justify your choice with a molecular orbital energy level diagram.

13. Use molecular orbital theory to explain why the Be_2 molecule does not exist.

14. Compare relative stability of the following species and indicate their magnetic properties (that is, diamagnetic or paramagnetic): O_2, O_2^+, O_2^- (superoxide ion), O_2^{2-} (peroxide ion).

15. Use molecular orbital theory to compare the relative stability of F_2 and F_2^+.

MOLECULAR POLARITY

16. How can a molecule be nonpolar if it contains polar bonds?

17. Compare the expected molecular polarities of H_2O and H_2S. Assume that both molecules have the same angle.

18. CO_2 is a nonpolar molecule, but CO is polar. Explain.

19. Compare the expected molecular polarities of CH_4 and CH_2F_2.

20. Compare the expected molecular polarities of $CHCl_3$ and CHF_3.

INTERMOLECULAR FORCIES

21. Define the following terms and give an example for each category: (a) dipole-dipole interaction, (b) ion-dipole interaction, (c) dispersion forces, (d) van der Waals forces.

22. Define hydrogen bonding. Which elements are able to take part in hydrogen bonding.

23. Why is ice less dense than water?

24. Ammonia is both a donar and an acceptor of hydrogen in hydrogen bond formation. Draw a diagram to show the hydrogen bonding of an ammonia molecule with two other ammonia molecules.

25. Which of the following species are capable of hydrogen bonding among themselves? (a) C_2H_6, (b) HI, (c) KF, (d) BeH_2, (e) CH_3COOH.

CHAPTER 15
COORDINATION (COMPLEX) COMPOUNDS

> *The chemical nature of a complex*
> *particle is determined by the nature,*
> *quantity and chemical structure*
> *of its elementary constituents.*
>
> *A. M. Butlerov*

After reading this chapter, you should be able to:

- define coordination compounds, complexing agents and ligands;
- describe classification of coordination compounds according to nature of their ligands;
- discuss naming of coordination compounds;
- describe bonding in coordination complexes using VB Method and Crystal-field Theory; define magnetic properties of coordination ions;
- discuss metal-ligands equilibrium in water solutions and stability of coordination compounds.

The broadest and most diverse class of inorganic substances includes the *coordination*, or *complex compounds*. They play an important role in nature, especially for elements of the d-block. In this chapter, we introduce the common structural arrangements of complexes, and then discuss the nature of the ligand-metal bonding in terms of two theoretical models. We start with the VB theory, and then progress to the crystal-field theory, which is based on an electrostatic model of the bonding.

15.1. Main definitions

Complex (coordination) compounds are defined as the compounds in which a covalent number of a central atom is greater than its ordinary covalence number.

For example: $FeCl_3$ is a simple compound, but $[FeCl_6]^{3-}$ is a coordination compound. Our understanding of the nature of coordination compounds is the result of the classic work of Alfred Werner.

Alfred Werner (1866–1919) studied in Karlsruhe, Zurich and Paris. He was a co-worker of Berthelot in Paris and a teacher of Organic Chemistry in Zurich. His more valuable work refers to the stereochemistry of nitrogen compounds. In 1893 he enunciated the theory of residual valences that made possible the discovery of isomers of many metallic combinations. Received the Nobel Prize of Chemistry in 1913.

According to Werner's theory, coordination compounds consist of:

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

- ligands (ions or polar molecules);
- ions of outer sphere (counter ions).

Central atoms are usually metals, and seldom nonmetals (for example, 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:

Oxidation number	Coordination number
+ 1	2
+ 2	4, 6
+ 3	4, 6
+ 4	6, 8

Ligands are ions or polar molecules that surround the metals in coordination ions. They contain one or several donor atoms bond directly to the metal ions. Ligands are classified according to the number of donor atoms.

We can distinguish **unidentate ligands** that form only one covalent bond with a complexing agent. They are:

(a) anions of monoprotic acids:

Cl^- — chloro;
Br^- — bromo;
I^- — iodo;
CN^- — cyano;
CNS^- — thiocyanato;
NO_2^- — nitro;

(b) some other anions:

OH^- — hydroxo;
H^- — hydrido;

(c) some simple molecules:

H_2O — aqua;
CO — carbonyl;
NH_3 — ammine;
NO — nitrosyl.

Bidentate ligands form two covalent bonds with the complexing agents. They are:

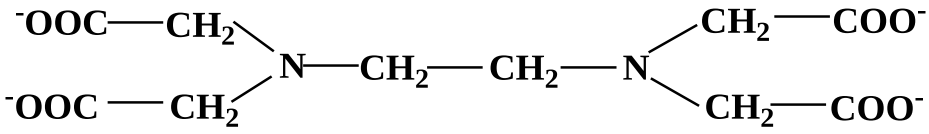
(a) anions of diprotic acids:

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

(b) some molecules:

$NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$ — ethylendiamine;
$NH_2\text{-}CH_2\text{-}COOH$ — glycine;

Polydentate ligands can form three, four, five and six covalent bonds with the complexing agents. For example, the chelating agent ethylenediaminetetraacetate (EDTA) is said to be one of the most powerful ligands able to form stable complex (coordinating) compounds.

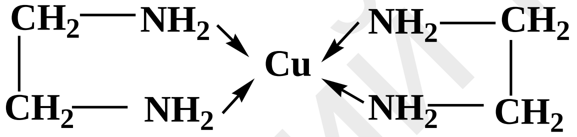


Its coordination numbers can take the values four and six.

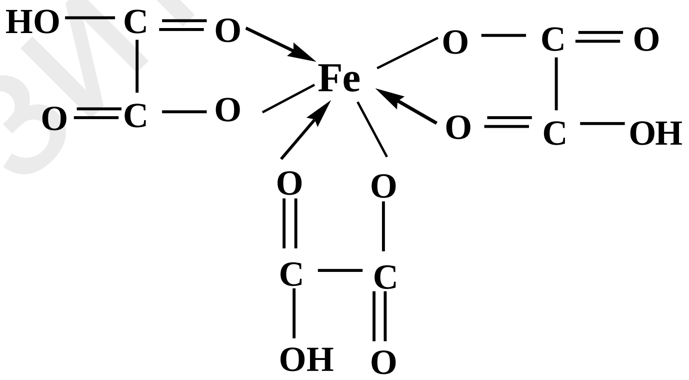
CLASSIFICATION OF COORDINATION COMPOUNDS

Complex compounds can be classified according to the nature of their ligands:

- aqua complexes: $[Cu(H_2O)_4]SO_4$;
- ammines: $[Ni(NH_3)_4]Cl_2$;
- hydroxyl complexes: $K_2[Zn(OH)_4]$;
- acido complexes: $K_4[Fe(CN)_6]$;
- carbonyls: $[Fe(CO)_5]$;
- complex compounds of a mixed type: $Na[Al(OH)_4(H_2O)_2]$;
- **chelate coordination compounds** (from the Greek *chele* means claw) — are complexes containing bi- or polydentate ligands, forming cycles. For example:



Intracomplex compounds are chelate complexes in which molecules the central atom is a part of a cycle and forms covalent bonds in two different ways. For example, the complex of Fe (III) with oxalic acid contains three iron-oxygen bonds formed by the donor-acceptor mechanism and three iron-oxygen bonds formed the coupling mechanism:



Such natural complexes as hemoglobin and chlorophyll are the bright examples of intracomplex compounds.

Another way to classify coordination compounds is according to their lability and inertness. Complexes that are thermodynamically unstable but survive for long periods (at least a minute) are called *inert*. Complexes that undergo more rapid equilibration are called *labile*. For example, all complexes of s-block ions are very labile. Inertness is quite common among the complexes of d-block metals.

15.2. Naming of coordination compounds

The rules for naming coordination compounds are the following:

(1) the cation is named before the anion, as in the case for other ionic compounds;

(2) in naming the complex ion the ligands are named first, in alphabetical order, and the metal ion is named last;

(3) 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), and NH_3 (ammine);

(4) 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 contains a Greek prefix, we use the prefixes bis-, tris-, and tetrakis to indicate the number of ligands present;

(5) the oxidation number of the metal is written in Roman numerals following the name of the metal;

(6) if the complex is an anion, its name ends in -ate (table 15.1).

Table 15.1 — Naming of metals

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

EXAMPLE 15.1. Name an oxidation and coordination numbers of central atoms in the following coordination compounds:

(a) $K_2[Fe(CN)_5NH_3]$;

(b) $[Co(H_2O)_4Cl_2]Cl$;

(c) $[Ni(CO)_4]$.

Give the systematic names 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: $x – 5 = –2$, where x is an oxidation number of the iron atom. Thus $x = +3$. A coordination number of the iron atom is six since it forms six covalent bonds with six monodentate ligands. The compound is called potassium pentacyanoammine ferrate (III).

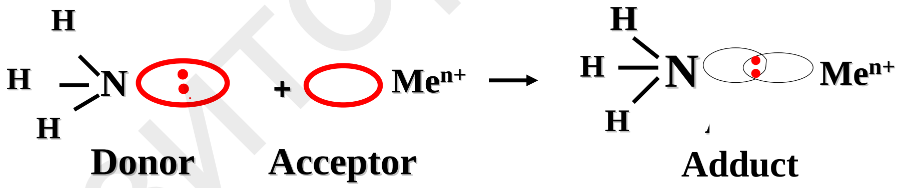
(b) The complex ion is a cation and it bears one positive charge. It contains two types of ligands: two chloride anion and four water molecules. An oxidation number of the cobalt atom may be calculated in a following way: $x - 2 = +1$, where **x** is an oxidation number of the cobalt atom. Thus $x =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

15.3. Bonding in coordination compounds

The formation of coordination compounds may come about either through a donor-acceptor 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 coordination compounds are formed through a donor-acceptor interaction mainly of the unpaired electron pairs of ligands and the vacant orbitals of the metal. The interaction of metals and ligands is represented by the following scheme:



The configurations of complex ions depend upon a type of hybridization of complexing agents and their coordination numbers (table 15.2).

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:

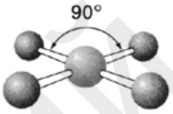
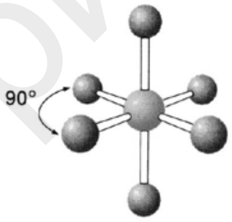
$$\mathbf{I^- > Br^- > Cl^- > F^- > OH^- > H_2O > NH_3 > En > NO_2^- > CN^- > CO}$$

Weak field Strong field

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. In figures 15.1 and 15.2 d-subshell splitting in octahedral and tetrahedral fields are represented respectively.

Table 15.2 — Common configurations of complex ions

Coordination number	Type of hybridization	Configuration	Examples
2	sp	linear	$[Ag(NH_3)_2]^+$
4	sp^3	tetrahedral	$[Zn(NH_3)_4]^{2+}$
	dsp^2	 square planar	$[AuCl_4]^-$
6	d^2sp^3 sp^3d^2	 octahedral	$[CoF_6]^{3-}$ $[Co(NH_3)_6]^{3+}$

The crystal-field splitting (Δ) depends upon the metals and ligands. When ligands' field is weak Δ 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 Δ 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).

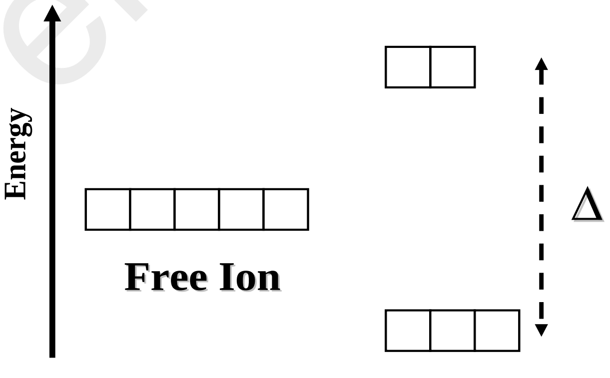


Figure 15.1 — d-Subshell splitting in octahedral field

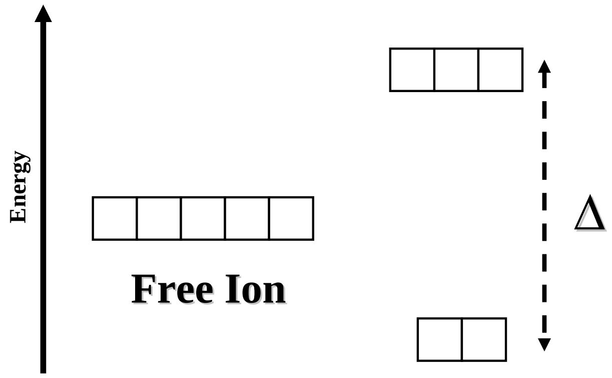


Figure 15.2 — d-Subshell splitting in tetrahedral field

The electrons distribution of Fe^{3+} ion during formation of the octahedral complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ is represented in figure 15.3.

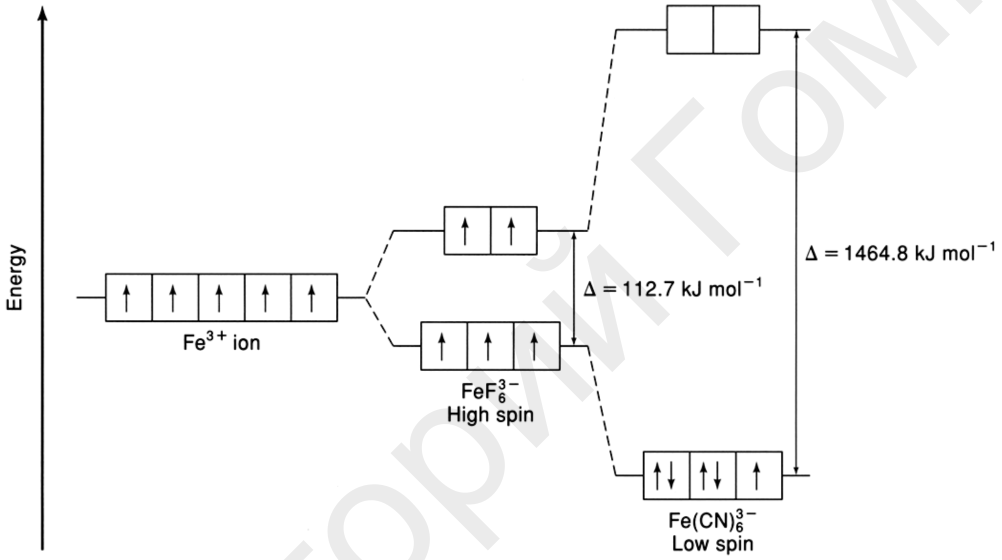


Figure 15.3 — Energy-level diagrams for $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$

Because F^- is a weak-field ligand with a small value of Δ, Hund's rule prevails, and $[FeF_6]^{3-}$ is a high-spin complex. The opposite holds true for the strong-field ligand CN^-. In $[Fe(CN)_6]^{3-}$ 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. High-spin complexes are paramagnetic while low-spin complexes are diamagnetic.

15.4. Stability of coordination compounds

According to their ability to dissociate in water solutions complex compounds fall into two categories: (a) electrolytes, and (b) non-electrolytes. As a rule complex non-electrolytes do not contain counter ions. For example, $[Pt(NH_3)_2Cl_2]$ is a non-electrolyte.

Dissociation of complex compounds that break down into ions in water solutions involves two steps:

- **primary dissociation**, which proceeds irreversibly as ionization of strong electrolytes:

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

- **secondary dissociation**, which proceeds reversibly as ionization of weak electrolytes:

$$[Fe(CN)_6]^{4-} \rightleftharpoons Fe^{2+} + 6CN^-$$

Metal-ligands equilibrium is characterized by equilibrium constant named the formation (stability) constant K_f:

$$K_f = \frac{[[Fe(CN)_6]^{4-}]}{[Fe^{+2}] \times [CN^-]^6} \qquad (15.1)$$

The formation constant is a measure of the stability of a complex: the higher K_f, the greater is stability of complex compounds. We can appreciate stability of complex compounds with the help of instability constant K_{ins}. **Instability constant** is reverse to formation constant:

$$K_{ins} = \frac{1}{K_f} \qquad (15.2)$$

In the example given above instability constant is calculated as:

$$K_f = \frac{[Fe^{+2}] \times [CN^-]^6}{[[Fe(CN)_6]^{4-}]} \qquad (15.3)$$

The instability constant is also a measure of the stability of a coordination compounds. The lower is K_{ins}, the greater is stability of complexes. For example, the silver complexes are arranged in a series according to the decrease in the values of their instability constants. Thus from the left to the right there is increase in their stability:

$[Ag(NO_2)_2]^-$	**$[Ag(NH_3)_2]^+$**	**$[Ag(CN)_2]^-$**
1.3×10^{-3}	**6.8×10^{-8}**	**1.0×10^{-21}**

$$\longrightarrow$$

increase in stability

Formation and instability constants indicate stability of complex compounds but they do not give reason for their stability. We can find the explanation for stability of complexes in their structure. It was proved that there are three main factors that effect stability of complex compounds. They are (a) ionic radii of complexing agents, (b) electric charge of metal ions and (c) the number of donor atoms in ligands.

The smaller are radii of metals and the higher are their electric charges, the greater is stability of complex ions. Thus stability of s-block metals' complexes is lower than stability of coordination compounds formed by p- and d-block metals because s-block metals exhibit large ionic radii and small electric charges (+1 and +2). Stability of d-block metals is high because they exhibit small ionic radii (the effect of d-compression). Stability of metal complexes increases in the following order:

$$\underrightarrow{\textbf{s-Me}\quad \textbf{p-Me}\quad \textbf{d-Me}}$$

Increase in complexing activity

Polydentane ligands form more stable coordination compounds than monodentate ligands. Especially stable are the chelates. This phenomenon is known as the *chelate effect***.** The chelate effect is the high stability of chelated complexes compared with their non-chelated analogs. This statement can be proved by the following data:

	K_{ins}
$[Co(NH_3)_4]^{2+}$	1.0×10^{-5}
$[Co(Gly)_2]$	3.3×10^{-9}
$[CoY]^{2-}$	1.0×10^{-16}

EXAMPLE 15.2. Write equations for primary and secondary dissociation of $K_2[HgI_4]$.Give the expression for its formation constant.

ANSWER:

(a) primary dissociation is represented by an equation:

$$K_2[HgI_4] \rightarrow 2\,K^+ + [HgI_4]^-$$

(b) secondary dissociation is given by:

$$[HgI_4]^{2-} \rightleftharpoons Hg^{2+} + 4\,{}^{-}I$$

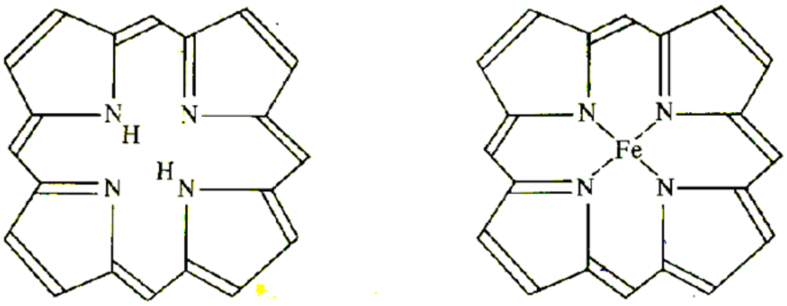
According to the Law of mass action formation constant (K_f) is:

$$K_f = \frac{[[HgI_6]^{2-}]}{[Hg^{+2}]\times[I^-]^4}$$

15.5. Biological functions of coordination compounds

In a human body all metals (except Na and K) are bounded into stable complexes with bioligands: amino acids, proteins, vitamins, hormones and other bioactive compounds. Most important are metal complexes with proteins. They are hemoglobin, chlorophyll and numerous metal enzymes. Hemoglobin is a protein made up of four nearly identical polypeptide chains each of which contains a coordination complex of iron (II). The Fe^{2+} in hemoglobin is bound to tetradentate porphyrin ligands (figure 15.4).

Porphyrin cycle is a chelating agent contained in a great number of bioactive compounds: hemoglobin, chlorophyll and cytochrome C which are involved in oxidation-reduction reactions in vivo (figure 15.5).



porphine Fe^{2+}-porhyrin

Figure 15.4 — Structure of the porphine molecule and the Fe^{2+}-porhyrin complex. The dotted lines indicate coordinate covalent bonds

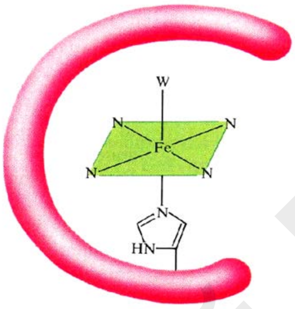
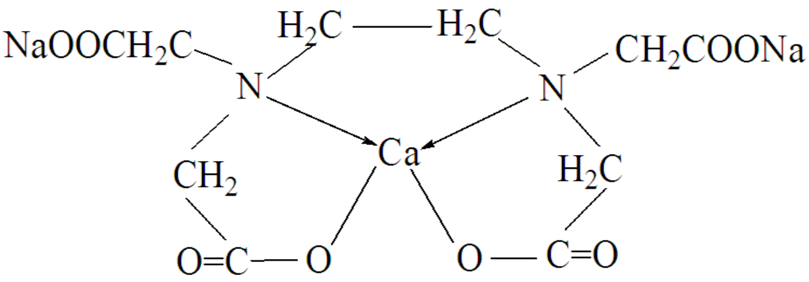


Figure 15.5 — The heme group in hemoglobin. The Fe^{2+} ion is coordinated with the nitrogen atoms of the heme group. The ligand below the porphyrin is the histidine group that attached to the protein

The balanced flow of metals and ligands into a biological system and out of it results in metal – ligand equilibrium or homeostasis. The disturbance of metal-ligand homeostasis *in vivo* results in different diseases. For example, iron deficiency is responsible for anemia, and its excess results in siderosis. The World Health organization reported that iron deficiency is the most common nutritional disorder in the world and that as many as 4–5 billion people, 66–80 % of the world's population, may be iron deficient. Iron deficiency is among the ten leading global risk factors and causes 800,000 (1.5 per cent) of deaths worldwide. Calcium deficiency is responsible for osteoporosis, and its excess results in cataracts and atherosclerosis.

Modern medicine widely applies complex compounds to correct metal-ligands homeostasis in a body and thus treat different diseases. The cis-isomer of [Pt $(NH_3)_2Cl_2$] has been used to control tumors and cancers. Its promise in this area was discovered during a study of the effect of an electric field on bacterial growth. Unexpectedly, it was found that minute amounts of the «*inert*» platinum electrodes form traces of coordination compounds that inhibit cell division in bacteria.

Some complexes of gold, for example $Na_3[Au(S_2O_3)_2]$, are used to treat tubercolosis and rheumatoid arthritis. The chelate complex of calcium with EDTA ligands, named *tetacine*, is applied to treat heavy metals poisoning:



Simplified formula of tetacine is $Na_2[CaY]$, and we shall use it to explain the therapeutic effect of this complex compound. For example, when a person is poisoned by mercury the following reaction runs in biological fluids:

$$Hg^{2+} + [CaY]^{2-} \rightleftharpoons Ca^{2+} + [HgY]^{2-}.$$

Mercury cations displace calcium in the inner sphere of a chelate complex since, as illustrated in Section 15.4, complexes of d-block metals are much more stable than complexes of s-block metals. The complex anion $[HgY]^{2-}$ is removed from the body by kidneys. Tetacine is also applied for detoxification when a person is poisoned with Pb, Cd and other heavy metals.

Chelating agents such as EDTA and its sodium salt are also applied to bind and remove toxic metals from a human body. A small amount of EDTA prevents lead cations from acting as catalysts for the oxidation of fats and oils that occur as these foods become spoiled or rancid. The effects of lead poisoning in children, a critical problem in run-down urban housing where old lead paint is still exposed, are relieved by treating patients with EDTA, which complexes the lead ion for elimination in the urine.

Chelating agents are applied to dissolve kidneys stones (to treat urolithiasis). Calcium stones account for 75-85% of urinary stones. Approximately one half of calcium stones are composed of a mixture of calcium oxalate and calcium phosphate (figure 15.6).

Figure 15.6 — Approximately three eighths of calcium stones are formed of only calcium oxalate dihydrate. The remaining one eighth of stones is composed of calcium phosphate (apatite) or calcium monohydrate. Uric acid stones account for 5–10 % of urinary stones

Calcium oxalate ($Ca_2C_2O_4$) which is a component of kidneys stones is readily dissolved in EDTA and its sodium salt Na_2H_2Y according to the equation:

$$Ca_2C_2O_4 + Na_2H_2Y \rightleftharpoons [CaY]^{2-} + Na_2C_2O_4 + 2\ H^+.$$

In the middle of 20th century *bioinorganic chemistry* was developed as a branch of chemistry dealing with structure, properties and biological functions of complex compounds which contain essential metals and bioactive ligands. The achievements of bioinorganic chemistry are wide used in medicine.

Coordination compounds are applied not only in medicine but in various branches of people activity. Some of the oldest practical uses of coordination compounds have been due to their colors. It is based on art and practice going back to the days of metal coordination chemistry. Complexes of iron (II) and iron (III) cyanides are still known by such names as Turnbull's blue, Prussian blue, and Berlin green. Blueprints are based on an iron cyanide complex. Recently, new dyes, especially those used on some of the synthetic fabrics that are difficult to tint, have been made from coordination compounds.

It was proved that coordinating ligands can influence greatly the available concentration of simple ions in solution. Phosphate chelating agents are used in water softeners to keep calcium ions in solutions; chelated iron is used in fertilizers to provide iron that will not react with soils to form insoluble iron compounds; and chelated metal ions can be formed that are more soluble in oil than in water — the reverse of the usual ionic behavior. Chelating agents are used to remove unwanted impurities from drinking water. They also have been used in separating the mixtures of metal ions found in the fission products of nuclear reactors. A complex containing aluminum and titanium is used as a catalyst in the making of polyethylene, one of the most important commercial processes discovered in this century.

The chelating agent ethylenediaminetetraacetate (EDTA) is said to be the most important modern analytical reagent. During the past 30 years, when most new analytical techniques have been based on electric and optical instruments, more than 100 research papers a year have appeared on the use of EDTA in «wet» chemical methods. One of its many other uses is in complexing traces of heavy metal ions in food.

15.6. Laboratory work

COORDINATION COMPOUNDS

Preparing of cationic complexes

TEST 1. Preparing of Cu (II) complex ammine

Treat 2–3 drops of copper (II) sulfate solution with some drops of sodium hydroxide solution and mark the color of copper (II) hydroxide precipitate. Dissolve a prepared precipitate in 1–2 mℓ of 25 % ammonia solution. Mark a color of a prepared solution. Give a systematic name to the prepared complex compound. Write the chemical equations of fulfilled reactions:

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

TEST 2. Preparing of Ni (II) complex ammine

Treat 2–3 drops of nickel (II) sulfate solution with some drops of sodium hydroxide solution and mark the color of nickel (II) hydroxide precipitate. Dissolve a prepared precipitate in 1–2 mℓ of 25 % ammonia solution. Mark a color of a prepared solution. Give a systematic name to the prepared complex compound. Write the chemical equations of fulfilled reactions:

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

Preparing of anionic complexes

TEST 3. Preparing of Bi (III) acido complex

Pour 3–4 drops of bismuth (III) nitrate solution into 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 a prepared solution? Give a systematic name to the prepared complex compound. Write the chemical equations of fulfilled reactions:

$$Bi\ (NO_3)_3 + 3\ KI \rightarrow BiI_3\downarrow + 3\ KNO_3$$
$$BiI_3 + KI \rightleftharpoons K\ [BiI_4]$$

TEST 4. Preparing of Hg (II) acido complex

Pour 3–4 drops mercury (II) nitrate solution into a test-tube and add some drops of potassium iodide solution 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 a prepared solution? Give a systematic name for the prepared complex compound. Write the chemical equations of fulfilled reactions:

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

Warning! All forms of mercury are toxic. Doing experiments with solutions of mercury salts you must avoid their contact with skin.

TEST 5. Preparing of hydroxyl complexes

Pour 3–4 drops of zinc, chromium and aluminum salts solutions into each of the three test-tubes and treat them with 2–3 drops of sodium hydroxide solution up to the formation of precipitates. Mark the color of prepared precipitates and dissolve them in the excess of alkali solution. Mark the color of prepared solutions and give systematic names for the hydroxyl complexes. Write the equations of the reactions:

$$ZnCl_2 + 2\ NaOH \rightarrow Zn\ (OH)_2\downarrow + 2\ NaCl$$
$$Zn\ (OH)_2 + 2\ NaOH \rightleftharpoons Na_2\ [Zn\ (OH)_4]$$

$$CrCl_3 + 3\ NaOH \rightarrow Cr\ (OH)_3\downarrow + 3\ NaCl$$
$$Cr\ (OH)_3 + 3\ NaOH \rightleftharpoons Na_3[Cr(OH)_6]$$

$$Al(NO_3)_3 + 3\ NaOH \rightarrow Al(OH)_3\downarrow + 3\ NaNO_3$$
$$Al(OH)_3 + NaOH \rightleftharpoons Na[Al(OH)_4]$$

TEST 6. Preparing of chelate coordination compounds

Pour 3 drops of iron (III) chloride solution into each of the three test tubes and treat two of them with 3 drops of NaOH solution. Mark the color of the prepared precipitate. Treat the precipitate in the first test tube with the excess of oxalic acid solution. Mark the color of a prepared solution. The precipitate in the second test tube treat with the the excess citric acid solution. Mark the color of a prepared solution.

Add 1–2 drops of NH_4CNS solution into each of the test tube, including a test tube filled by initial $FeCl_3$ solution. Mark the color of all prepared solutions. Does red-blood color appear in all the test tubes? Write the chemical equations of fulfilled reactions. Make a conclusion about stability of chelate complex compounds.

Stability of coordination compounds

TEST 7. Stability of silver coordination compounds

Treat 2–3 drops of silver (I) nitrate solution with some drops of sodium chloride solution and mark the color of silver (I) chloride precipitate. Dissolve the precipitate in 1–2 mℓ of 25 % ammonia solution. Mark the color of a prepared solution. Add some drops of potassium iodide solution into a test-tube with the prepared solution. Mark the color of an obtained precipitate. Compare K_{sp} of AgI and K_f of $[Ag(NH_3)_2]^+$. Make a conclusion about stability of silver compounds. Give a systematic name to the prepared complex compound. Write the chemical equations of fulfilled reactions:

$$2\ AgNO_3 + 2\ NaOH \rightarrow Ag_2O\downarrow + 2\ NaNO_3 + H_2O$$
$$Ag_2O + 4\ NH_4OH \rightleftharpoons 2\ [Ag(NH_3)_2]OH + 3\ H_2O$$
$$[Ag(NH_3)_2]OH + KI \rightleftharpoons AgI\downarrow + 2\ KOH + 2\ NH_3\uparrow$$

TEST 8. Stability of thiocyanate coordination 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 the color of a prepared solution and give a systematic name for an obtained complex compound. Separate a solution into two test tubes. Add 3–5 drops of amyl alcohol ($C_5H_{11}OH$) 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 chemical equations of a fulfilled reaction:

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

TEST 9. Stability of aluminum coordination compounds

Prepare a solution of sodium tetrahydroxoaluminate (III) (Test 5) and add 5–6 drops of NH_4Cl saturated solution. Mark a color of a prepared precipitate. Make a conclusion about stability of aluminum complex compounds. Write the chemical equations of fulfilled reactions:

$$Al(NO_3)_3 + 4\ NaOH \rightleftharpoons Na[Al(OH)_4] + 3\ NaNO_3$$
$$Na[Al(OH)_4] + 3\ NH_4Cl \rightleftharpoons Al(OH)_3\downarrow + 3\ NaCl + 3\ NH_4OH$$

15.7. Problems

DISCUSSION QUESTIONS

1. Define the following terms: coordination compounds, ligands, donor atoms, coordination number, chelating agent.

2. Distinguish between unidentane, bidentate and polydentate ligands. Give the examples.

3. Explain such a phenomenon as chelate effect. Give the examples of chelate complexes.

4. Define the following terms: crystal field splitting, high-spin complex, spectrochemical series.

5. What factors determine whether a given complex will be diamagnetic or paramagnetic?

6. Distinguish between labile and inert complexes.

7. Describe medical application of coordination compounds.

8. What chelate coordination compounds are essential to life?

NUMERICAL EXERCISES

1. Calculate charges of the following complex ions. Add ions of outer sphere. Give their systematic names.

(a) $[Ni^{2+}(CN)_4]$;(b) $[Cr^{3+}(NH_3)_6]$;

(c) $[Zn^{2+}(OH)_4]$;(d) $[Cu^{2+}(H_2O)_4]$;

(e) $[Pt^{4+}(NH_3)_4Cl_2]$;(f) $[Co^{3+}(CN)_4Br_2]$.

2. Calculate the electric charges of complexing agents in the following coordination compounds. Give their systematic names.

(a) $K_2[PtBr_4]$;(b) $Na_4[Fe(CN)_6]$;

(c) $[Pb(NH_3)_6]Cl_4$;(d) $[Cu(H_2O)_4]SO_4$;

(e) $[Cr(NH_3)_5Cl]Cl_2$;(f) $K[Co(H_2O)_2(NO_2)_4]$;

(g) $[Cr(NH_3)_3(H_2O)_3]Cl_3$.

3. Give a definition for the formation constant. Write an equation for $[Fe(CN)_6]^{3-}$ ionization and mathematical equation for its K_f and K_{ins}.

4. Write formulas of the following coordination compounds:

(a) pentaamminechloroplatinum (IV) chloride

(b) potassium tetrahydroxochromate (III)

(c) hexaammincobalt (III) bromide

5. The $[Ni(CN)_4]^{2–}$ ion, which has square-planar geometry, is diamagnetic, whereas the $[NiCl_4]^{2–}$ ion, which has tetrahedral geometry, is paramagnetic. Show the crystal-field splitting diagrams for those two complexes.

6. Predict the number of unpaired electrons in the following complex ions: (a) $[Cr(CN)_6]^{4-}$ and (b) $[Cr(H_2O)_6]^{2+}$.

7. The label of a certain brand of mayonnaise lists EDTA as a food preservative. How does EDTA prevent the spoilage of mayonnaise?

CHAPTER 16
CHEMISTRY OF BIOESSENTIAL ELEMENTS

> *Only when thinking got down to the relationships between*
> *the separate atoms in particles, i.e. when the hypothesis*
> *of structure was developed, was light shed on reality*
> *so that it became clearly conceivable.*
>
> *A. M. Butlerov*

After reading this chapter, you should be able to:

- classify chemical elements according to their electronic configurations;
- derive electron configurations of the s-, p- and d-block elements and their simple ions;
- discuss the alteration of metallic and non-metallic properties of elements across the periods and down the groups;
- explain the alteration of acid-base properties of oxides and hydroxides across the periods and down the groups;
- determine the properties of elements hydrogen compounds;
- specify bioessential elements and discuss their content and biological functions in a human body;
- write the equations of test reactions for ions of s-, p- and d-block elements.

The four parts of this chapter lay the foundations of the chemistry of bioessential elements. The first part develops an understanding of the main statements of biogeochemistry. The following three parts develop the description of the electronic configurations and chemical properties of s-, p- and d-block elements and their compounds. Special attention is focused on biological functions of bioessential elements and application of their compounds in medicine.

16.1. The bases of biogeochemistry

Biogeochemistry is a branch of chemistry which deals with distribution of chemical elements and their migration in biosphere. A linkage between living and non-living matter is a key problem of biogeochemistry. Biogeochemistry was developed in the 30-th of XX century by Russian academic Vladimir Vernadsky.

Biosphere is an area of our planet composed of all living entities on Earth. It includes lithosphere, hydrosphere and atmosphere composed of troposphere and stratosphere. Academician Vernadsky came to belief that qualitative composition of earth crust and biomass is approximately identical, but their quantitative composition is quite different. It was proved that 98 per cent of the earth crust is composed of eight chemical elements such as oxygen, silicon, aluminum, iron, calcium, sodium, potassium and magnesium. Another six elements predominate in living matter: carbon, hydrogen, oxygen, nitrogen, phosphorus and sulfur. They built up 97.4 per cent of a body mass. As you can see metals predominate in the earth crust and non-metals are favored in living systems. The chemical elements abundance in different geospheres is presented in table 16.1.

Vladimir Vernadsky (1863–1945) was a Russian and Soviet mineralogist and geochemist who is considered one of the founders of geochemistry, biogeochemistry, and of radiogeology. His ideas of noosphere were an important contribution to Russian cosmism. He also worked in Ukraine where he founded the National Academy of Science of Ukraine. He is most noted for his 1926 book **The Biosphere** in which he inadvertently worked to popularize Eduard Suess' 1885 term biosphere, by hypothesizing that life is the geological force that shapes the earth.

Table 16.1 — Chemical Elements abundance in different geospheres

№	Chemical Element	Hydrosphere	Lithosphere	Biomass
1	O	85.82	47.2	62.4
2	H	10.72	0.15	9.80
3	Cl	1.89	0.045	0.15
4	Na	1.06	2.64	0.15
5	Mg	0.14	2.1	0.05

Among chemical elements widely spread in living matter only oxygen and calcium are abundant in the earth crust. Such elements as silicon, aluminum and iron that are widely spread in the earth crust are presented in biomass only in low concentrations.

According to professor Vinogradov theory, living systems accumulate mainly those chemical elements that form gases and vapors of atmosphere or water soluble compounds with the main ions of hydrosphere (such as H^+, $OH^–$, $HCO_3^–$, $CO_3^{2–}$, $I^–$, $SO_4^{2–}$ and $PO_4^{3–}$). **For example,** carbon is a macroelement in all living systems, because it forms gaseous oxides CO and CO_2, but silicon is a microelement since SiO_2 is a solid substance insoluble in water. The chemical elements that are contained in biomass and fulfill some biological functions are defined as **bioessential elements**. The main bioessential elements are:

- six non-metals: C, O, H, N, P, S;
- ten biometals (metals of life): Na, K, Mg, Ca that are s-block elements, and Fe, Co, Cu, Zn, Mn, and Mo that are d-block elements.

According to their content in biomass chemical elements fall into three categories:

(a)**macroelements** (their content is greater than $10^{–2}$ per cent by mass);

(b) **microelements** (their content is in the range $10^{–5}$–$10^{–3}$ per cent by mass);

(c) **ultramicroelements** (their content less than $10^{–5}$ per cent by mass).

The list of macroelements involves seven non-metals, such as carbon, oxygen, nitrogen, phosphorus, sulfur, hydrogen and chlorine, and four metals: sodium, potassium, calcium and magnesium. Zinc, copper, iron, cobalt, manganese, molybdenum, nickel, chromium, silicon, boron and many other elements are defined as microelements, while mercury, gold, francium and some others are contained in living systems only in trace amounts (they are ultramicroelements).

There is a relationship between content of an element in a human body and its position in the Periodic Table. In groups the toxicity of elements and their compounds increases from top to bottom, and as the result their amount in biomass decreases. The list of toxic metals is presented in table 16.2.

Table 16.2 — High Toxic Metals

IV A	**V A**	**VI A**	**VII A**	**VIII**			**I B**	**II B**
	V*	**Cr ***	**Mn**	**Fe**	**Co**	**Ni ***	**Cu**	**Zn**
Zr	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd ***
Hf	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg ***

*Extremely toxic metals.

The toxicity of an element depends upon its oxidation state in a chemical compound. The higher is oxidation state of an element the greater is its toxicity. For example, the ions Cr^{3+} exhibit low toxicity but the anions CrO_4^{2-} and $Cr_2O_7^{2-}$, that contain Cr^{6+}, exhibit extremely high toxicity.

Vinogradov Aleksandr Pavlovich (1895–1975) is academician, geochemist, vice-president of the Academy of Sciences of the USSR.

The relationship between bioessential microelements in the environment and health disturbance is already known, but mostly connected with acute poisoning due to the increased concentration in human body. However, recently the concept of the effects of bioelement deficiency has started to be more important. A.P.Vinogradov developed a concept of biogeochemical province.

Biogeochemical province is an area of biosphere which is distinguished by extremely high or extremely low content of one or several chemical elements and endemic diseases of population as a response.

16.2. S-block elements

GENERAL FEATURES OF THE S-BLOCK ELEMENTS

On the basis of the modern quantum-mechanical interpretation of the periodic table classification of the chemical elements is produced in accordance with their electronic configuration.

s-block		d-block										p-block					
IA	IIA											IIIA	IVA	VA	VIA	VIIA	VIIIA
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IB	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt				Uut	Uug		Uuh		Uuo

f-block													
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 16.1 — Periodic Table of Chemical Elements

s-Block elements are chemical elements that exhibit electronic configuration $\mathbf{ns^x}$, where **x** is a number of electrons in s-subshell, and **n** is a principal quantum number. The numerical values for **x** are one or two. s-Block elements are the main groups' elements. Most of them are metals, known as **alkali** (IA group) and **alkaline earth** (IIA group). Only hydrogen and helium are nonmetals.

Before we study specific metals, let us look at the general properties of metallic elements. Their atoms are distinguished by large atomic radii and small number of outer electrons. Because metals generally have low electronegativities, they tend to form cations and almost always have positive oxidation numbers in their compounds. As the electronegativity of the main groups elements increases from left to right across a period and from bottom to top in a group, the metallic properties of elements increase from right to left across a period and from top to bottom in a group.

The Alkali Metals (Group IA) are the most electropositive (or the least electronegative) elements known. In other words they are the most active metals and can easily donate one electron, turning into a cation with the charge +1:

$$\mathbf{Me - e^- \rightarrow Me^+}.$$

The common electronic configuration of alkali metals is responsible for their numerous similar properties. Table 16.3 lists some common properties of the alkali metals.

Table 16.3 — Physiochemical properties of Alkali Metals (The Group IA elements)

Element	**Content in earth's crust, % by mass**	**Electronic configuration ns^1**	**Atomic radius, nm**	**Ionization potential, eV**	**Standard reduction potential, V**
Li	6.5×10^{-3}	[He]$\mathbf{2s^1}$	0.155	5.39	-3.05
Na	2.5	[Ne]$\mathbf{3s^1}$	0.189	5.14	-2.71
K	2.6	[Ar]$\mathbf{4s^1}$	0.236	4.34	-2.93
Rb	1.5×10^{-2}	[Kr]$\mathbf{5s^1}$	0.248	4.17	-2.93
Cs	3.7×10^{-4}	[Xe]$\mathbf{6s^1}$	0.268	3.89	-2.92
Fr	—	[Rn]$\mathbf{7s^1}$	0.280	3.98	—

From top to bottom their orbital radii increase, electronegativity and ionization potentials decrease. Thus the metallic character increases in the same direction. From their electronic configuration we expect the oxidation number of these elements in their compounds to be +1 since the cations would be isoelectronic with the noble gases.

Because of their great chemical reactivity, the alkali metals never occur naturally in elemental form; they are found combined with halide, sulfate, carbonate, and silicate ions. Their main compounds are *oxides* (Me_2O) and *hydroxides* (MeOH), which are basic by nature. Oxides are readily dissolved in water and acids forming bases and salts respectively:

$$Na_2O + H_2O \rightarrow 2\ NaOH$$
$$Na_2O + 2\ HCl \rightarrow 2\ NaCl + H_2O$$

Their hydroxides are strong bases; they are 100 per cent ionized in water:

$$NaOH \rightarrow Na^+ + OH^-$$

They are readily neutralized by acids:

$$2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O$$

Their basicity increases from top to bottom according to the rule: the increase in metallic activity of elements gives rise to the increase of oxides and hydroxides basic properties.

Hydrogen compounds of alkali metals (MeH) are classified as *saline hydrides*. They are non-volatile, electrically non-conducting, crystalline solids that contain hydride anion $H^–$ in their structure. The reactions provide chemical evidence for the existence of $H^–$. The reactions of saline hydrides with water and acids are dangerously vigorous:

$$NaH + H_2O \rightarrow NaOH + H_2,$$
$$NaH + HCl \rightarrow NaCl + H_2.$$

Sodium and potassium are most abundant in nature among other alkali metals; they are considered to be bioessential elements of living matter. Their content in a human body is greater than $1\times10^{–2}$ per cent by mass thus they are **macroelements**. **Potassium** is an essential element for plants and animals. In higher animals potassium ions together with sodium ions act at cell membranes in transmitting electrochemical impulses in nerve and muscle fibers and in balancing the activity of food intake and waste removal from cells. Potassium also is necessary for protein synthesis, fluid balance and muscle contraction. Potassium deficiency causes weakness, paralysis, mental confusion, and possible death. Excessive intake of potassium can result in muscular weakness, and possible vomiting. Estimated minimum requirements are 2000 mg/day for adults and adolescents. Food sources of potassium are fruits, vegetables, dairy, grains, legumes, and beef. The content of potassium in some food products is given in table 16.4.

Table 16.4 — The content of potassium in some food products

Food	Potassium, mg/100g	Food	Potassium, mg/100g
Dried apricots	1780	Beef	350
Kidney beans	1100	Cod	340
Prunes, raisins	860	Apples	250
Peas	730	Bread	210
Potatoes	570	Curd	110

Sodium is an essential element in the human body. Life could not exist without compounds of sodium. These compounds hold water in body tissues, and a severe deficiency of sodium can cause death. Sodium compounds also adjust acid-base balance and are involved in nerve impulse transmission. Blood contains sodium compounds in solutions. Deficiency of sodium causes cramping, apathy, depressed appetite. Excessive intake of sodium may cause a hypertension. Recommended intakes of sodium are no more than 2,400 to 3,000 mg/day. Minimums: 500 mg/day for adults and 120 mg for infants. Food sources of sodium compounds are table salt or sodium chloride (NaCl), soy sauce, pickled foods, canned foods, many processed foods.

The content of lithium, rubidium and cesium is approximately 1.0×10^{-5} per cent by mass, so they are **micro elements**. **Lithium**, even although its role in human body is not well known yet, makes a big difference in our well being. Its deficiency causes abnormalities in brain development, various mental disorders, like depression or aggression. It is being tested in treating alcohol and drug dependencies.

Rubidium has been investigated for its antidepressant effect in a group of psychiatric disorders.

Cesium can be taken into the body by eating food, drinking water, or breathing air. After being taken in, cesium behaves in a manner similar to potassium and distributes uniformly throughout the body. Gastrointestinal absorption from food or water is the principal source of internally deposited cesium in the general population. Essentially all cesium that is ingested is absorbed into the bloodstream through the intestines. Cesium tends to concentrate in muscles because of their relatively large mass. Cesium is under laboratory investigation for its role in carcinogenesis and in depressive illness. Very little is known of **francium** due to its great instability for experimental study.

Hydrogen is the most abundant element in the universe. In fact, hydrogen makes up an estimated 90 percent of all atoms. In most cases, when you hear about hydrogen, it is usually in the context of outer space, military weapons or fuel sources for cars. However hydrogen is also a crucial element in the operation of the human body. One of the major ways that hydrogen is used in the body is in water. Water is so important that it makes up over 60 percent of your body. Because of hydrogen, the cells are able to remain hydrated, toxins and waste are able to be eliminated from the body, nutrients are able to be transported to the cells that need them, joints are lubricated, and body’s immune system is able to send defensive cells to fight of infection-causing fungus, bacteria and viruses.

Hydrogen also plays a crucial role in energy production in the body. For our bodies to function, they must have energy in the form of adenosine triphosphate (ATP). A body gains energy through consuming foods rich in substances such as carbohydrates. Once ingested, the body uses enzymes to break down your food into more basic substances such as glucose. These basic parts are then further broken down through glycolysis and beta oxidation, leaving a body with acetyl CoA. Acetyl CoA is then broken down into hydrogen, oxygen and carbon. The hydrogen ions are transported to the mitochondria of the cells, which then uses the hydrogen to create ATP. Hydrogen is the missing link in slowing down the aging process. The aging of tissues in the body is believed to be caused by substances called free radicals in the body. Inside many of the tissues in the body are stored (pooled) supplies of hydrogen. According to Dr. Flanagan, this hydrogen protects us from free radical damage. Unfortunately, as we age, these storages dry up. This leaves the tissue exposed to free radicals, which leads to the tissue damage seen with aging.

The concentration of hydrogen ions (H^+) effects the pH of different body fluids. Gastric juice has a low pH due to many hydrogen ions, which helps to break down food. Hydrogen ions in the body effect our breathing rate (a lower pH increase our breathing rate). Also, pH effects the activity of enzymes.

Hydrogen bonds are important to the body for several reasons. For one thing, they cause DNA to retain its double helix structure. Additionally, they contribute to the folding of proteins, which is necessary for proper protein function. The main biological functions of some alkali metals and application of their compounds in medicine are given in appendix table 5.

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:

- soft, but harder than alkali metals;
- reactive, but not as reactive as alkali metals;
- ionization energies are not as low as alkali metals;
- salts less soluble than those of the alkali metals.

Table 16.6 lists some common properties of these metals.

Table 16.5 — The Alkaline Earth Metals (The Group IIA elements)

Symbol	Content in earth's crust, % by mass	Electron configuration, ns^2	Atomic radius, nm	Ionization potential, eV	Standard reduction potential, V
Be	6×10^{-4}	$[He]2s^2$	0.112	9.32	-1.84
Mg	2.1	$[Ne]3s^2$	0.160	7.64	-2.36
Ca	3.6	$[Ar]4s^2$	0.197	6.11	-2.86
Sr	4×10^{-2}	$[Kr]5s^2$	0.215	5.69	-2.88
Ba	5×10^{-2}	$[Xe]6s^2$	0.222	5.21	-2.91
Ra	1×10^{-10}	$[Rn]7s^2$	0.280	5.27	-2.91

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 **MeH_2.**

Oxides and hydroxides of alkaline earth metals are basic, except BeO and $Be(OH)_2$, that exhibit amphoteric (amphiprotic) properties. Beryllium compounds are soluble both in acids and bases:

$$Be(OH)_2 + 2\ HCl \rightarrow BeCl_2 + 2\ H_2O,$$
$$Be(OH)_2 + 2\ NaOH \rightarrow Na_2\,[Be(OH)_4].$$

From top to bottom with the increase in elements metallic properties there is an increase in basicity of their oxides and hydroxides.

The hydrogen compounds of alkaline earth metals are saline hydrides (MeH_2), that are readily decomposed by water and acids:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2,$$
$$CaH_2 + 2HCl \rightarrow CaCl_2 + H_2.$$

Calcium and magnesium are bioessential elements of living matter. Their content is a human body is more than 1×10^{-2} % by mass thus they are **macroelements**.

Calcium refers to the chemical elements plentifully necessary for a person's oganism and animals. The biological role of calcium is rather diverse: it is the basic structural component of bones, cartilages and teeth (97–99 %). Its rest part is contained in plasma of blood, muscles, a liver, a pancreas, kidneys and other organs in the ioized and connected condition. Calcium takes part during nervous and muscular fabric’s excitation, in the blood coagulability system functioning, in the cellular membrane permeability regulation. It supports nervously — muscular tone, sexual function preservation, and also an organism’s steadiness to the external adverse factors harmful influence, including the infectious diseases. Calcium supervises a number of important fermentation processes, promotes the prevention of diabetes and other diseases. Calcium deficiency can result in a range of health problems: osteoporosis, stunted childhood growth, possible hypertension and colon cancer. A adult person should receive from 800 up to 1100 mg of calcium every day with foodstuff and water, and for 14–18 years — about 1400 mg, for pregnant women — 1500 mg, for feeding mothers — 1800–2000 mg daily. The best sources of calcium are milk and hard cheese. Others are leafy greens, nuts, and small fishes such as sardines with bones that can be eaten. The content of calcium in some food products is given in table 16.6.

Magnesium is an essential element in the human body. It is necessary for bone mineralization, protein synthesis, enzymatic reactions, muscular contraction, and nerve transmission. Deficiencies of magnesium are rare in non-disease state; prevalent in chronic alcoholism, renal dysfunction, hyperparathyroidism. Symptoms of deficiency are weakness, confusion, hypertension, arrhythmia, depressed pancreatic hormone secretion, growth failure, behavioral disturbances, muscle spasms. The content of calcium and magnesium in some food products is given in table 16.6.

Table 16.6 — The content of calcium and magnesium in some food products

Food	Calcium, mg/100g	Food	Magnesium, mg/100g
Hard cheese	1040	Peas	107
Yolk of egg	140	Millet	83
Milk	120	Buckwheat	78
Kale, broccoli	110	Hard cheese	56
Oatmeal	70	Bread	35–80
Buckwheat	40	Beef	22
Bread	30–50	Milk	13
Beef	10	Apples	9

Beryllium, strontium and barium are **microelements. Beryllium** is highly toxic especially if inhaled as a dust. When you breathe in large amounts of soluble beryllium compounds, the lung damage resembles pneumonia with reddening and swelling of the lungs. This condition is called acute *beryllium disease*. Some people can become sensitive to beryllium. This is known as hypersensitivity or allergy. If you become sensitive (allergic) to beryllium, you will develop an immune or inflammatory reaction to amounts of beryllium that do not cause effects in people who are not sensitive to beryllium.

Strontium is absorbed by the bone like calcium because of its compositional similarity. The stable strontium substances don't pose a threat. In fact, there is currently a drug produced that combines ranelic acid with strontium; it aides in bone growth and denser bones, and lessens vertebral, peripheral and hip fractures. Sr-90, a radioactive isotope, can cause cancer in high doses. Research has registered that the element Sr-90 is partly a cause of several types of cancer including leukemia, bone nose, lung and skin.

Unlike that of strontium, **barium's** toxicity to the human body is chemical rather than radioactive in nature. If taken into the body as a soluble salt (for example, $BaCl_2$), barium causes serious deterioration of the heart's function – a phenomenon known as *ventricular fibrillation.* Interestingly, the insoluble barium sulfate, $BaSO_4$, is nontoxic to humans, presumable because of the low Ba^{2+} ion concentration in solutions. This dense barium salt absorbs X rays and acts as an opaque barrier to them. Thus, X-ray examination of a patient who has swallowed a solution containing finely divided $BaSO_4$ particles allows the radiologist to diagnose an ailment of the patient's digestive tract. Barium sulfate is quite insoluble ($K_{sp} = 1.1\times10^{-10}$), so it passes through the digestive system and no appreciable amounts of Ba^{2+} ions are taken up by a body.

The main biological functions of some alkaline earth metals and application of their compounds in medicine are given in Appendix table 6.

16.3. Laboratory work

QUALITATIVE REACTIONS ON THE CATIONS OF S-BLOCK METALS

Qualitative analysis is used to separate and detect cations and anions in a sample substance. In an educational setting, it is generally true that the concentrations of the ions to be identified are all approximately 0.01 M in an aqueous solution. The semi micro level of qualitative analysis employs methods used to detect 1–2 mg of an ion in 5 mℓ of solution. **Qualitative reaction** is followed by an analytical effect: precipitation, color changing or gas elimination.

TEST 1. Qualitative reaction on К$^+$

1. Sodium hexanitrocobaltate (III) $Na_3\,[Co(NO_2)_6]$ interacts with potassium cations with the formation of yellow crystals of potassium-sodium hexanitrocobaltate (III) according to the reaction:

$$2\,KCl + Na_3\,[Co(NO_2)_6] \rightarrow K_2Na\,[Co\,(NO_2)_6]\downarrow + 2\,NaCl$$
$$2K^+ + Na^+ + [Co(NO_2)_6]^{3-} \rightarrow K_2Na\,[Co\,(NO_2)_6]\downarrow$$

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

$$[Co(NO_2)_6]^{3-} + 3\,OH^- \rightarrow Co(OH)_3\downarrow + 6\,NO_2^-$$
$$[Co(NO_2)_6]^{3-} + 10\,H^+ \rightarrow 2\,Co^{2+} + 5\,NO + 7NO_2 + 5\,H_2O$$

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:

$$KCl + NaHC_4H_4O_6 \rightarrow KHC_4H_4O_6\downarrow + NaCl$$
$$K^+ + HC_4H_4O_6^- \rightarrow KHC_4H_4O_6\downarrow$$

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:

$$KCl + H_2C_4H_4O_6 + CH_3COONa \rightarrow KHC_4H_4O_6\downarrow + NaCl + CH_3COOH$$

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

$$KHC_4H_4O_6\downarrow + HCl \rightarrow H_2C_4H_4O_6 + KCl$$
$$KHC_4H_4O_6\downarrow + KOH \rightarrow K_2C_4H_4O_6 + H_2O$$

Moreover, 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$^+$

Potassium hexahydroxostibiate (V) 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 (V) solution. What can you see?

TEST 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:

$$2\,MgCl_2 + 2\,(NH_4)_2CO_3 + H_2O \rightarrow (MgOH)_2CO_3 \downarrow + CO_2 \uparrow + 4\,NH_4Cl$$
$$Mg^{2+} + 2\,CO_3^{2-} + H_2O \rightarrow (MgOH)_2CO_3 \downarrow + CO_2 \uparrow$$

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:

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

$Mg(OH)_2$ is readily dissolved in acids and ammonium salts:

$$Mg(OH)_2 + 2\,H^+ \rightarrow Mg^{2+} + 2\,H_2O$$
$$Mg(OH)_2 + 2\,NH_4^+ \rightarrow Mg^{2+} + 2\,NH_4OH$$

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_4Cl и HCl solutions.

3. Sodium hydrophosphate 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_4Cl и NH_4OH 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^{+2}

1. Ammonium carbonate $(NH_4)_2CO_3$ interacts with barium salts with the formation of a $BaCO_3$ white precipitate:

$$BaCl_2 + (NH_4)_2CO_3 \rightarrow BaCO_3 \downarrow + 2\,NH_4Cl$$
$$Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3 \downarrow$$

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:

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2\ HCl$$
$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$$

$BaSO_4$ is insoluble in strong acids.

Pour 3 drops of $BaCl_2$ solution and 3 drops of a dilute H_2SO_4. 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:

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

A reaction is carried out with the addition of CH_3COONa, 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 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:

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + 2\ NH_4Cl$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow$$

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

Pour 3 drops of $CaCl_2$ solution and 3 drops of a $(NH_4)_2CO_3$ 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:

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2\ NH_4Cl$$
$$Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4 \downarrow$$

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) $K_4\ [Fe\ (CN)_6]$ interacts with calcium salts' solutions with the formation of white crystals of $Ca\ (NH_4)_2[Fe\ (CN)_6]$. A reaction is carried out in the presence of an ammonium buffer system (a mixture of NH_4OH and NH_4Cl):

$$CaCl_2 + 2\ NH_4Cl + K_4[Fe(CN)_6] \rightarrow Ca(NH_4)_2[Fe(CN)_6] \downarrow + 4\ KCl$$
$$Ca^{2+} + 2\ NH_4^+ + [Fe(CN)_6]^{4-} \rightarrow Ca(NH_4)_2[Fe(CN)_6] \downarrow$$

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 6. 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:

$$Sr^{2+} + (NH_4)_2CO_3 \rightarrow SrCO_3 \downarrow + 2\ NH_4^{+}$$

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

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

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 $CaSO_4{\cdot}2H_2O$ (gypsum water) interacts with strontium salts' solutions with the formation of white crystals of strontium sulfate:

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

Heating may accelerate a reaction.

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

16.4. Problems for the self-control

DISCUSSION QUESTIONS

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

(a) Na and Na^{+} (c) Sr and Sr^{2+}
(b) Ca and Ca^{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 lay at the bottom of bone tissue formation.

4. Specify which of the following systems can be classified as a buffer system: (a) $NaCl/HCl$; (b) $Mg(NO_3)_2/HNO_3$; (c) $KHCO_3/K_2CO_3$; (d) $HCOOLi/HCOOH$.

5. Write the equations for the following salts hydrolysis:

(a) KF (c) $Mg(NO_3)_2$
(b) Li_2CO_3 (d) Na_3PO_4

6. Use table 16.8 «Presentation of an element» to describe calcium and magnesium.

NUMERICAL EXERCISES

1. Barium cations are toxic. Which of the following barium salt is more harmful if ingested: $BaCO_3$ or $BaSO_4$? Explain. Calculate solubility of these salts in moℓ/ℓ and g/ℓ. $K_{sp}(BaCO_3) = 5.0\times10^{-9}$, $K_{sp}(BaSO_4) = 1.1\times10^{-10}$.

Answer: 7.1×10^{-5} M or 1.39×10^{-2} g/ℓl;
1.05×10^{-5} M or 2.44×10^{-3} g/ℓ

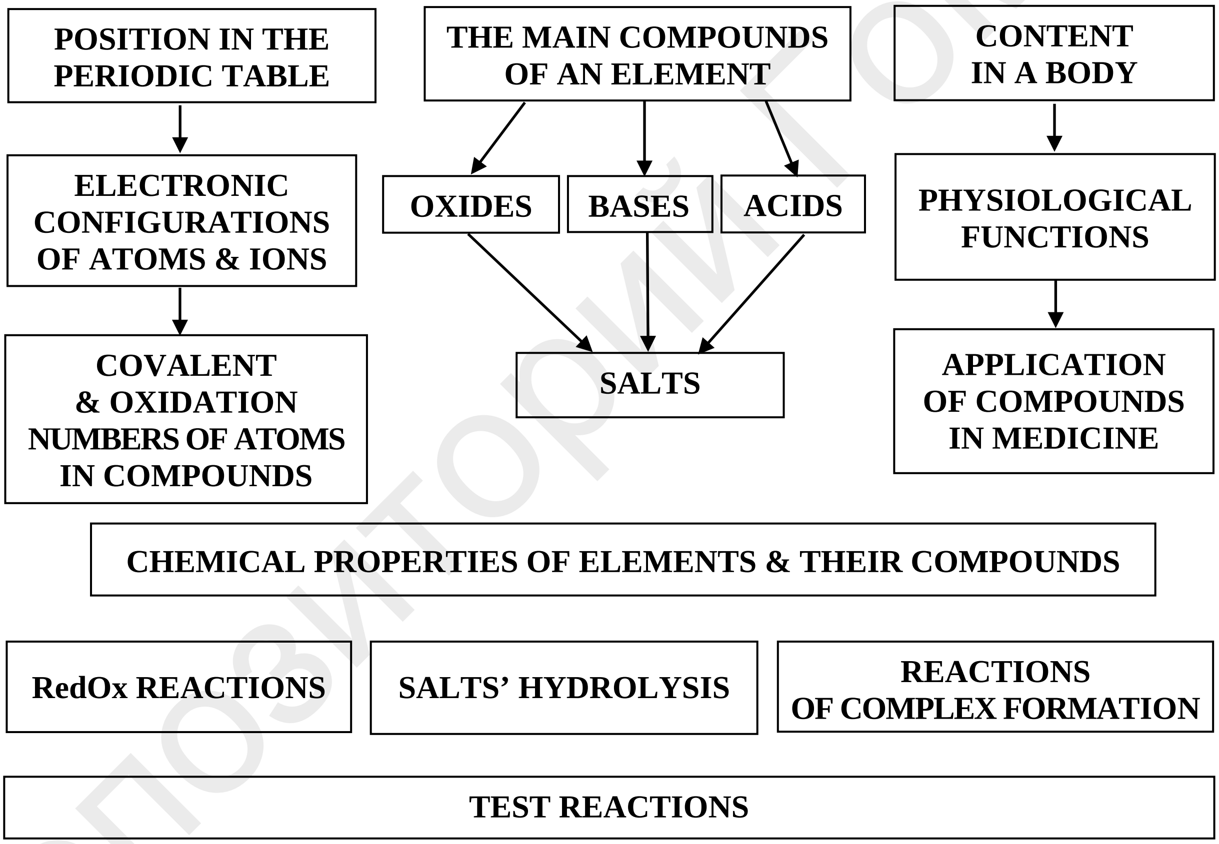
2. A buffer solution is prepared by mixing 500 mℓ of 0.15 M $NaHCO_3$ and 500 mℓ 0.10 M Na_2CO_3 (pK_a of HCO_3^- = 10.4). (a) Calculate the pH of the buffer solution. (b) Write a balanced chemical equation that shows what happens when 0.4 grams of NaOH is added to a buffer solution. What is the pH of the solution after the addition of NaOH?

Answer: 10.22; 10.37

3. The osmotic pressure of NaCl solution is 350 kPa at 25 °C. Calculate per cent by mass concentration of a salt in a given solution, taking into consideration that ionization degree of a salt is 0.95. Discuss the possibility of the solution application in medicine. Assume that density of a solution is 1.0 g/ℓ.

Answer: 0.42 %

Table 16.7 — Presentation of an element

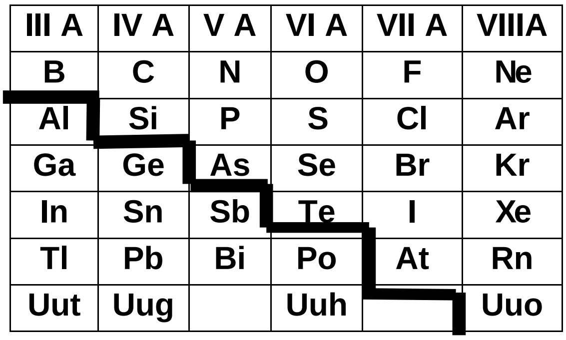


16.5. p-Block elements

GENERAL FEATURES OF THE p-BLOCK ELEMENTS

p-Block elements are characterized by ns^2np^x electronic configurations, where ***x*** is a number of electrons in the p-subshell. It takes the numerical values from one to six.

p-Block chemistry is a little complicated compared to the s-block chemistry. The reason behind this is that p-block not only has non-metals, but metals too. A diagonal borderline from boron to astatine separates p-block elements into metals and non-metals. Non-metals are located up the borderline, and metals are located down it (figure 16.2). p-Block elements are the main groups elements. They are located in groups IIIA–VIIIA. The elements of each group are electronic analogues thus they exhibit similar chemical properties.



III A	IV A	V A	VI A	VII A	VIIIA
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn
Uut	Uug		Uuh		Uuo

Figure 16.2 — p-Block elements

The groups of the p-block are:
IIIA: Boron group;
IVA: Carbon group;
VA: Nitrogen group;
VIA: Chalcogens;
VIIA: Halogens;
VIIIA: Noble gases.

The physiochemical properties of p-block elements show certain regularity in periods and groups. From left to the right there is a decrease in atomic radii and increase in ionization potentials of atoms, their electronegativity and electron affinity. In groups from top to bottom there is an increase in atomic radii and decrease in ionization potentials of atoms, their electronegativity and electron affinity (table 16.9).

Table 16.8 — Periodic trends in alteration of physiochemical properties in p-block elements

Properties	**Along a period (left to right)**	**Down a group (top to bottom)**
Atomic radii: size of an atom	Decreases	Increases with addition of a main orbital
Ionization potentials: energy required to remove valence shell electron	Increases	Decreases
Electronegativity : tendency of an atom to attract shared pair towards itself	Increases	Decreases
Electron affinity: amount of energy released when an electron is added to an atom	Increases	Decreases

The illustrations of these tendencies you can find in tables 16.10–16.12. They contain numerical values about physiochemical properties in the third period and in groups of boron and halogens.

Table 16.9 — Physiochemical properties of the third period

Element	Al	Si	P	S	Cl	Ar
Electronic configuration	[Ne] $3s^23p^1$	[Ne] $3s^23p^2$	[Ne] $3s^23p^3$	[Ne] $3s^23p^4$	[Ne] $3s^23p^5$	[Ne] $3s^23p^6$
Atomic radii, nm	0.143	0.134	0.130	0.104	0.099	0.192
Ionization potential, eV	5.99	8.15	10.5	10.4	13.0	15.8
Electro negativity	1.47	1.74	2.10	2.60	2.83	3.20
Electron affinity, eV	0.20	1.36	0.80	2.08	3.61	-0.37

Table 16.10 — Physiochemical properties of the IIIA group elements

Element	**Electronic configuration ns^2np^1**	**Atomic radius, nm**	**Ionization potential, eV**	**Electro negativity**	**Electron affinity, eV**
B	[He]$\mathbf{2s^22p^1}$	0.091	8.30	2.01	0.30
Al	[Ne] $\mathbf{3s^23p^1}$	0.143	5.99	1.47	0.50
Ga	[Ar] $\mathbf{4s^24p^1}$	0.139	6.00	1.82	0.39
In	[Kr] $\mathbf{5s^25p^1}$	0.166	5.79	1.49	0.20
Tl	[Xe] $\mathbf{6s^26p^1}$	0.171	6.11	1.44	0.50

Table 16.11 — Physiochemical properties of the VIIA group elements

Element	**Electronic configuration ns^2np^5**	**Atomic radius, nm**	**Ionization potential, eV**	**Electro negativity**	**Electron affinity, eV**
F	[He]$\mathbf{2s^22p^5}$	0.04	17.42	4,10	3.45
Cl	[Ne] $\mathbf{3s^23p^5}$	0.073	12.97	2,83	3.61
Br	[Ar] $\mathbf{4s^24p^5}$	0.085	11.84	2,74	3.37
I	[Kr] $\mathbf{5s^25p^5}$	0.105	10.45	2.21	3.08
At	[Xe] $\mathbf{6s^26p^5}$	0.115	9.20	1,90	2.81

Analyzing the data given above we come to belief that metallic properties of atoms decrease from left to right across the period, and non-metallic properties increase in the same direction. The elements of VIIA group (halogens) are most active non-metals. The metallic properties of atoms increase down each group and nonmetallic properties decrease in the same direction.

Most p-block elements can adopt more than one oxidation states. In periods the maximum oxidation states have a tendency to increase except elements of the second period. For most elements the maximum oxidation state is equal to the group’s number, but for oxygen it is only +2, and for fluorine -1. The oxidation states of the fourth period elements are given in table 16.12. Common oxidation states are in bold print.

The most important compounds of p-block elements are *oxides*, *hydroxides* and *hydrogen compounds*.

Table 16.12 — Variable oxidation states of the fourth period elements

Al	**Si**	**P**	**S**	**Cl**	**Ar**
+3	**+4**	**+5**	**+6**	**+7**	**No compounds are formed**
	+2	+4	**+4**	+6	
	-4	**+3**	+2	**+5**	
		+1	**-2**	+4	
		-3		**+3**	
				+1	
				-1	

Most non-metals oxides are acidic but few of them (e.g. CO, N_2O, NO and SiO) are non-salt-forming or indifferent. Most metal oxides are amphoteric except Bi_2O_3, which is basic. The acidity of oxides increases from left to right across the period in accordance with the rule: *the greater activity of a non-metal, the higher acidity of its oxide and hydroxide.* The same rule explains why acidity of oxides falls down the groups.

The oxidation state of an element is also responsible for the character of its oxide. Usually acidity of oxides increases with the increase in oxidation state of elements. Let us prove these theoretical concepts by examining the properties of Group VA Elements oxides (table 16.13).

The non-metals hydroxides are oxygen containing or oxyacids while metals hydroxides are amphoteric bases, except $Bi(OH)_3$,which has a basic nature.

Across the period the acidic properties of hydroxides become stronger and basic properties become weaker. In other words, hydroxides exhibit the same tendency as oxides do (table 16.14).

Table 16.13 — The properties of Group VA Elements oxides

Oxidation state	**Oxide**	**State of aggregation**	**Acid-base properties**
+1	N_2O	Colorless gas	Non-salt-forming
+2	NO	Colorless gas	Non-salt-forming
+3	N_2O_3	Blue liquid	↑ Acidic
	P_2O_3	White wax-like substance	Acidic
			Acidic
	As_2O_3	Colorless crystalline substance	
	Sb_2O_3	Colorless crystalline substance	Amphoteric
	Bi_2O_3		Basic
+4	NO_2	Yellow crystalline substance	Acidic
	N_2O_5	Reddish-brown gas	↑ Acidic
+5	P_2O_5	Colorless crystals	Acidic
	As_2O_5	White powder	Acidic
	Sb_2O_5	White vitreous substance	Acidic
	Bi_2O_5	Yellowish powder	Acidic
		Reddish-brown powder	

Note. The arrows in the last column indicate the directions of the increase in the acidic properties.

Table 16.14 — The properties of Period III Elements hydroxides

Hydroxide	$Al(OH)_3$	H_2SiO_3	H_3PO_4	H_2SO_4	$HClO_4$
Naming	Aluminum hydroxide	Silicic acid	Orthophosphoric acid	Sulfuric acid	Perchloric acid
Acid-base properties	Amphoteric base	Weak acid	Weak acid	Strong acid	Strong acid
Acid ionization constant	4.0×10^{-13}	2.2×10^{-10}	7.52×10^{-3}	1.0×10^{3}	1.0×10^{10}

→ **Increase in acidity**

The oxidation states of elements effect the character of hydroxides in the same way as they effect the character of oxides: their acidity increases with the increase in oxidation state of elements. Table 16.15 presents some properties of VA Group elements hydroxides that are of great practical use.

Table 16.15 — Properties of VA Group element hydroxides

Oxidation state	**Hydroxides**	**Naming of hydroxides**	**Acid-base properties**	**Acid ionization constant**
+1	H_3PO_2	Hypophosphorous acid	↑ Weak acid	8.5×10^{-2}
+3	HNO_2	Nitrous acid	Weak acid	5.0×10^{-4}
	H_3PO_3	Phosphorous acid	Weak acid	8.0×10^{-3}
	$HAsO_2$	Arsenous acid	Weak acid	6.0×10^{-10}
	$xSb_2O_3\times yH_2O$	Sb(III) hydroxide	Amphoteric base	1.0×10^{-11}
	$Bi(OH)_3$	Bi(III) hydroxide	Weak base	—
+5	HNO_3	Nitric acid	↑ Strong acid	21.0
	H_3PO_4	Phosphoric acid	Weak acid	0.011
	H_3AsO_4	Arsenic acid	Weak acid	6.0×10^{-3}
	$xSb_2O_5\times yH_2O$	Antimonic acid	Weak acid	4.0×10^{-5}

Note. The arrows in the last column indicate the directions of the increase in the acidic properties.

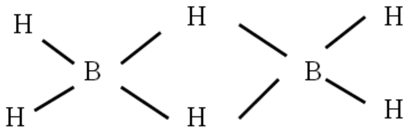
p-Block elements *hydrogen compounds* are of molecular type. They are binary compounds of an element and hydrogen in the form of individual, discrete molecules. Molecular compounds of hydrogen are common for the electronegative elements of Groups IIIA–VIIA, and examples include B_2H_6, CH_4, NH_3, H_2O, and HF. Most hydrogen compounds of p-block elements are gases under normal conditions, with different solubility in water.

It is convenient to classify molecular compounds of hydrogen into three categories:

- *electron precise compounds* — all valence electrons of the central atom are engaged in bonds;
- *electron-deficient compounds* — there are too few electrons to be able to write a Lewis structure for the molecule;
- *electron-rich compounds* — there are more electron pairs on the central atom than are needed for bond formation.

The hydrocarbons, such as methane CH_4 and ethane C_2H_6, are electron precise; so too are silane SiH_4 and germane GeH_4. All these molecules are characterized by the presence of two center, two electron bonds and the absence of lone pairs on the central atom.

Diborane B_2H_6 is an example of an electron-deficient compound. As we can see from its structural formula, 16 electrons are required to bind the eight atoms together, but the molecule has only 12 valence electrons:



The simple explanation of its structure is the presence of **B – H – B** bonds, acting as bridges between the two B atoms, so two electrons can help to bind three atoms. Electron-deficient hydrogen compounds are common for boron and aluminum.

Electron-rich compounds are formed by the elements in Groups VA through VIIA. Ammonia NH_3 with one electron pair on nitrogen, and water H_2O with two lone electron pairs on oxygen, are examples. The hydrogen halides HF, HCl, HBr and HI are another important group of electron-rich compounds.

According to acid-base theory, developed by Bronsted and Lowry (see chapter 11.1), electron-rich hydrogen compounds fall into two categories:

- proton donors or bases (VA Group elements);
- proton acceptors or acids (VIA and VIIA Groups elements).

The physical properties of VA and VIIA Groups elements hydrogen compounds are presented in tables 16.16 and 16.17.

Table 16.16 — Properties of VA Group element hydrides

Compound	**NH_3**	**PH_3**	**AsH_3**	**SbH_3**
Naming	Ammonia	Phosphine	Arsine	Stibine
State of aggregation	Colorless gas	Colorless gas	Colorless gas	Colorless gas
Solubility in water	31 % (25 °C)	31.2 mg/100 mℓ (17 °C)	0.07g/100 mℓ (25 °C)	Insoluble
Basicity constant	1.78×10^{-5}	4.0×10^{-28}	—	—

Decrease in basicity

Table 16.17 — Properties of VIIA Group element hydrides

Compound	**HF**	**HCl**	**HBr**	**HI**
Naming	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide
State of aggregation	Colorless gas	Colorless gas	Colorless gas	Colorless gas
Solubility in water	Miscible	67.3 g/100 mℓ (30 °C)	193 g/100 mℓ (20 °C)	234 g/100 mℓ (10 °C)
Acid ionization constant	7.2×10^{-4} weak acid	1.0×10^{7} strong acid	1.0×10^{9} strong acid	1.0×10^{11} strong acid

Increase in acidity

Oxidation states of elements effect not only acidity and basicity of oxides and hydroxides, but oxidation and reduction properties of their compounds. The increase in oxidation state of the atom, as a rule, leads to an increase in its oxidative capacity.

EXAMPLE 16.1. Explain how oxidation and reduction properties of nitrogen compounds change in a series: $\mathbf{N^{-3} \rightarrow N^{+3} \rightarrow N^{+5}}$. Prove your conclusions with the help of chemical reactions.

Answer:

The oxidation state -3 is the lower oxidation state of nitrogen thus an atom exhibits only reductive property. We can prove this statement by writing the equation of ammonia oxidation by oxygen:

$$NH_3 + O_2 \quad N_2 + H_2O$$

$$\begin{array}{r|l} 2\,N^{-3} - 3e \rightarrow N_2 & 4 \\ O_2 + 4e \rightarrow 2\,O^{-2} & 3 \end{array}$$

The oxidation state +3 is the intermediate oxidation state for nitrogen hence an atom exhibits redox duality. Thus, the salts of nitrous acid can act both as oxidizing and reducing agents. For example, $NaNO_2$ is readily oxidized by $KMnO_4$:

$$NaNO_2 + KMnO_4 + H_2SO_4 \rightarrow NaNO_3 + MnSO_4 + K_2SO_4 + H_2O$$

$$\begin{array}{l|l} N^{+3} - 2e \rightarrow N^{+5} & 5 \\ Mn^{+7} + 5e \rightarrow Mn^{+2} & 2 \end{array}$$

Simultaneously this salt can be reduced by KI:

$$2\,NaNO_2 + 2\,KI + 2\,H_2SO_4 \rightarrow 2\,NO + I_2 + K_2SO_4 + Na_2SO_4 + 2\,H_2O$$

$$\begin{array}{l|l} N^{+3} + 1e \rightarrow N^{+2} & 2 \\ 2\,I^{-1} - 2e \rightarrow I_2 & 1 \end{array}$$

The oxidation state +5 is the highest oxidation state for nitrogen hence an atom acts as oxidizing agent only. Thus nitric acid is able to oxidize metals, non-metals and complex compounds. For example, it easily oxidizes phosphorus into phosphoric acid:

$$5\,HNO_3 + 2\,P + 2\,H_2O \rightarrow 3\,H_3PO_4 + 5\,NO$$

$$\begin{array}{l|l} N^{+5} + 3e \rightarrow N^{+2} & 5 \\ P^{0} - 5e \rightarrow P^{+5} & 3 \end{array}$$

Five p-block elements, such as oxygen, nitrogen, carbon, sulfur and phosphorus, play an essential role in a human body. They and chlorine are macro elements.

Oxygen enters our body as a gas with two oxygen atoms attached to each other to make one molecule of oxygen. The average adult at rest inhales and exhales something like 7 or 8 liters of air per minute. That totals something like 11,000 liters of air in a day. The air that is inhaled is about 21 percent oxygen, and the air that is exhaled is about 15-percent oxygen, so about 5 percent of the volume of air is consumed in each breath and converted to carbon dioxide. Therefore, a human being uses about **550 liters of pure oxygen** per day. As air moves into the lungs, small sacs called alveoli are inflated. Capillaries surround each sac and force the red blood cells to flow nearly single file while each blood cell drops off its load of carbon dioxide and picks up oxygen. From the lungs, the oxygen is transported by arterial blood to every cell in the body. In the tissues of the body, the blood cells again pass through another series of capillaries where they drop off oxygen and pick up carbon dioxide for their return trip to the lungs. **Cellular processes require oxygen to burn the calories from food.** The general process that cells use to turn food into energy is called respiration. Respiration is the opposite of photosynthesis. What plants do in photosynthesis to convert energy into sugar, respiration does in reverse to change sugar into energy. Within the cell, this operation is driven by a circular sequence called the citrus acid cycle or the Krebs cycle. This process stores energy in a molecule called adenosine triphosphate (ATP) when it is synthesized from adenosine diphosphate (ADP). The operation ultimately uses oxygen and creates carbon dioxide and water.

Cells use the ATP anytime that energy is required. When ATP is converted back to ADP, energy is released and the ADP is recycled along with the extra phosphate back into the system to be remade into ATP. It is the presence of oxygen that allows the body to use this food to energy conversion process. This happens essentially the same way in nerves, muscles, the heart, and all body tissues. When deprived of oxygen, cellular respiration eventually comes to a halt, and the cell will die. Oxygen is a component in many of the molecules in the human body. Amino acids which are the building blocks of proteins have oxygen in them. Consequently, proteins also have oxygen as part of their molecular structure. The same is true of carbohydrates and fats. Since these molecules comprise most of the tissue in the body, oxygen is a vital component to materials that comprise the body itself.

Sulfur represents about 0.25 percent of our total body weight, similar to potassium. The body contains approximately 140 grams of sulfur-mainly in the proteins, although it is distributed in small amounts in all cells and tissues. Sulfur is present in four amino acids: methionine, an essential amino acid; the non-essential cystine and cysteine, which can be made from methionine; and taurine, which is not part of body tissues but does help produce bile acid for digestion. Sulfur is also present in two B vitamins, thiamine and biotin; interestingly, thiamine is important to skin and biotin to hair. Sulfur is also available as various sulfates or sulfides. But overall, sulfur is most important as part of protein. It also plays an important part in the protection of joints. As well as this it maintains the balance of oxygen in the body and keeps skin, hair and nails healthy. Another thing, is that it plays a rather important role in producing collagen, a type of protein found in connective tissue, keratin and hair. Sulfur is also used to treat skin diseases, rheumatism, gout, bronchitis and prevents constipation.

Phosphorus is an important constituent in every body tissue. The total amount constitutes about one per cent of the body weight. The amount of phosphorus in the body is exceeded only by calcium. In bones the proportion of calcium to phosphorus is much higher than that of calcium. Most of this phosphorus is in organic combinations. Phosphorus is one element that performs a number of important functions. It combines with calcium to form a relatively insoluble compound calcium phosphate, which gives strength and rigidity to bones and teeth.

Phosphorus like calcium is needed not only for the growth of skeleton but also for its maintenance. The utilization of many nutrients that enter the body involves the formation and degradation of phosphorus containing compounds. The phosphorus-containing lipoprotein facilitates the transport of fats in the circulation. A series of phosphorus compound are formed in the utilization of carbohydrates in the body. It is vital to the fundamental process of metabolism in the body. Phosphorus is a constituent of the nucleoproteins the substances that control heredity.

Carbon is perhaps the single most important element to life. Virtually every body part contains large amounts of this element. The carbon atom is ideal to build big biological molecules. The carbon atom can be thought of as a basic building block. These building blocks can be attached to each other to form long chains, or they can be attached to other elements. This can be difficult to imagine at first, but it may help to think about building with Legos. You can think of carbon as a bunch of red legos attached together to form one long chain of legos. Now, you can imagine sticking yellow, blue and green legos across the tops of the red (carbon) legos. These other colors represent other elements like oxygen, nitrogen or hydrogen. As you stick more and more of these yellow, blue and green legos to the red chain, it would start to look like a skeleton of legos with a «spine» of red legos and «bones» of yellow, blue and green legos. This is a lot like the way that big molecules are made in the body. Without carbon, these big molecules could not be built. Now, virtually every part of your body is made up of these big molecules that are based around chains of carbon atoms. This is the reason we are known as «carbon based life forms». Without carbon, our bodies would just be a big pile of loose atoms with no way to be built into a person.

Nitrogen is essential macroelement in the human body; it is needed to make up amino acids, which in turn make up proteins. It is also needed to make vitamins and nucleic acids DNA and RNA. It is used to make carbohydrates. It plays an important role in digestion of food and growth. As you may know, almost 80 % of the air we breathe is made up of nitrogen. But humans cannot use the nitrogen in the air we breathe, that nitrogen is in the wrong form. We have to get nitrogen, in a different form, from the food that we eat. Fortunately, there is plenty of nitrogen in food to nourish our bodies. Nitrogen is found in large amounts in all kinds of food. Spaghetti, salads, breakfast cereal, hamburgers and even cookies have lots of nitrogen in the form that our bodies need. When your body digests this food and makes it into energy, the first step is to remove nitrogen atoms from the molecules in the food. While your body is busy digesting the rest of this food and making it into energy, these nitrogen atoms are already being used to help you grow. One specific time that this is especially important is during pregnancy. When a woman is pregnant, the nitrogen removed from food during digestion is needed to help the fetus to grow properly. By term, the mother and infant will have accumulated over a pound of nitrogen. It is also worth noting that in the plant kingdom, nitrogen is one of the 3 main elements that make plant life possible.

NO is an important regulator and mediator of numerous processes in the nervous, immune and cardiovascular systems. These include vascular smooth muscle relaxation, resulting in arterial vasodilatation and increasing blood flow. NO is also a neurotransmitter and has been associated with neuronal activity and various functions like avoidance learning. NO also partially mediates macrophage cytotoxicity against microbes and tumor cells. Besides mediating normal functions, NO is implicated in pathophysiologic states as diverse as septic shock, hypertension, stroke, and neurodegenerative diseases. Currently, exogenous NO sources constitute a powerful way to supplement NO when the body cannot generate enough for normal biological functions. So, recent developments of novel NO donors, NO releasing devices as well as innovative improvements to current NO donors have been investigated.

The brief information about biological functions and medical application of p-block elements and their compounds is given in Appendix table 7 and table 8.

16.6. Laboratory work

QUALITATIVE REACTIONS ON THE CATIONS OF p-BLOCK METALS

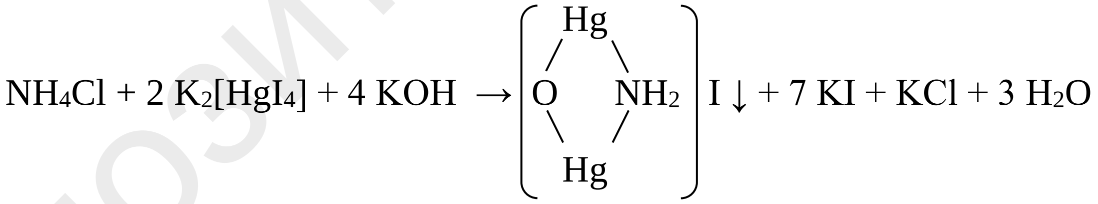
TEST 1. Qualitative reactions on NH_4^+

1. Ammonium salts' solutions interact with alkalis with ammonia gas elimination:

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

Pour some drops of NH_4Cl 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:



$$NH_4Cl + 2\,K_2[HgI_4] + 4\,KOH \rightarrow \left[\begin{array}{ccc} & Hg & \\ / & & \backslash \\ O & & NH_2 \\ \backslash & & / \\ & Hg & \end{array}\right] I\downarrow + 7\,KI + KCl + 3\,H_2O$$

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?

Warning! All forms of mercury are toxic. Doing experiments with solutions of mercury salts you must avoid their contact with skin.

TEST 2. Qualitative reactions on Al^{3+}

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

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

Add 5–6 drops of NaOH solution to the prepared precipitate. What can you see?

$$Al(OH)_3 + NaOH \rightleftharpoons Na[Al(OH)_4]$$

Add 5 drops NH_4Cl 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^{2+}

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 prepared 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?

$$SnCl_2 + 2\ NaOH \rightarrow Sn(OH)_2\downarrow + 2\ NaCl$$
$$Sn(OH)_2 + 2\ NaOH \rightleftharpoons Na_2[Sn(OH)_4\ ]$$
$$Bi(NO_3)_3 + 3\ NaOH \rightarrow Bi(OH)_3 + 3\ NaNO_3$$
$$2\ Bi(OH)_3 + 3\ Na_2[Sn(OH)_4] \rightarrow 2\ Bi\downarrow + 3\ Na_2[Sn(OH)_6]$$

TEST 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 prepared 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^{3+}

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 prepared 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?

$$SnCl_2 + 2\ NaOH \rightarrow Sn(OH)_2\downarrow + 2\ NaCl$$
$$Sn(OH)_2 + 2\ NaOH \rightleftharpoons Na_2[Sn(OH)_4\ ]$$
$$Bi(NO_3)_3 + 3\ NaOH \rightarrow Bi(OH)_3 + 3\ NaNO_3$$
$$2\ Bi(OH)_3 + 3\ Na_2[Sn(OH)_4] \rightarrow 2\ Bi\downarrow + 3\ Na_2[Sn(OH)_6]$$

Qualitative reactions on the anions of p-block nonmetals

TEST 6. Qualitative reactions on 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?

$$Na_2CO_3 + 2\ HCl \rightarrow 2\ NaCl + CO_2\uparrow + H_2O$$

TEST 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 $AgNO_3$ solution. What can you see?

$$2\ Na_2HPO_4 + AgNO_3 \rightarrow Ag_3PO_4\downarrow + 3\ NaNO_3 + NaH_2PO_4$$

TEST 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:

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \rightarrow Na_2SO_4 + 4\ H_3BO_3$$
$$H_3BO_3 + 3\ C_2H_5OH \rightarrow (C_2H_5O)_3B + 3\ H_2O$$

Put H_3BO_3 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^-

Pour 3 drops of $AgNO_3$ solution into a test tube and add 2 drops of NaCl solution. What can you see? Add NH_4OH solution up to formation a colorless solution:

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
$$AgCl\downarrow + 2\ NH_4OH \rightleftharpoons [Ag(NH_3)_2]Cl + 2\ H_2O$$
$$[Ag(NH_3)_2]Cl + KI + 2\ H_2O \rightarrow AgI\downarrow + 2\ NH_4OH + KCl$$

Separate a 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^-

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?

$$Pb\ (CH_3COO)_2 + 2\ KI \rightarrow PbI_2\downarrow + 2\ KCH_3COO$$
$$2\ I^- + Pb^{2+} \rightarrow PbI_2\downarrow$$

TEST 11. Qualitative reactions on NO_3^-

Diphenylamine $(C_6H_5)_2NH$ in the concentrated sulfuric acid is a reagent to determine NO_3^- anions. What can you see?

TEST 12. Qualitative reactions on NO_2^-

1. Pour 4–5 drops of $NaNO_2$ 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 $NaNO_2$ solution into a test tube and add 5–6 drops of dilute of H_2SO_4 solution. Then add solution $KMnO_4$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_3COO^-

Pour 2–3 drops of $FeCl_3$ solution into a test tube and add 1–2 drops of solution CH_3COONa. What can you see?

$$3\ CH_3COONa + FeCl_3 \rightleftharpoons Fe(CH_3COO)_3 + 3\ NaCl$$

16.7. Problems for the self-control

DISCUSSION QUESTIONS

1. Use table 16.7 «Presentation of an element» to describe bioessential elements nitrogen and phosphorus.

2. Discuss the biological functions of sulfur, oxygen and carbon in vivo.

3. Complete the following oxidation-reduction reactions and balance them using half-reaction method:

(a) $KMnO_4 + Na_2SO_3 + H_2SO_4 \rightarrow$

(b) $HBr + H_2SO_4 \rightarrow$

(c) $KMnO_4 + H_2S + H_2SO_4 \rightarrow$

(в) $P + HNO_3 \rightarrow$

4. Write the equations for the following salts hydrolysis:

(a) NaF	(b) Na_2CO_3
(c) Pb $(CH_3COO)_2$	(d) $Cr_2(SO_4)_3$

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

6. Define amphoteric hydroxides. Write equations of chemical reactions, which are applied to prove amphoteric nature of $Pb(OH)_2$ and $Sb(OH)_3$.

7. Draw a molecular orbital energy level diagram for the O_2 molecule. Compare its stability with stability of O_2^+ which can be prepared by bombarding the O_2 molecule with fast-moving electrons. Predict (a) magnetic character and (b) bond order of O_2.

8. Concentrated sulfuric acid reacts with sodium iodide to produce molecular iodine, hydrogen sulfide, and sodium hydrogen sulfate. Write a balanced equation for the reaction.

NUMERICAL EXERCISES

1. Carbonic acid H_2CO_3 is a weak diprotic acid that is ionized in water mainly by the first step. Its K_a is 3.0×10^{-7}. Calculate its ionization degree (α) in 0.10 M solution. What is the pH in a given solution? Assume only the first step of ionization.

Answer: $\alpha = 0.173$ %, pH =3.76

2. Use the standard reduction potentials to find equilibrium constants for each of the following reactions at 25 °C (Appendix II, table 14):

(a) $Cl_2(g) + 2\,Br^-(aq) \rightleftharpoons 2\,Cl^-(aq) + 2\,Br_2(\ell)$

(b) $3\,SO_3^{2-}(aq) + 2\,IO_3^-(aq) + \rightleftharpoons 5\,SO_4^{2-}(aq) + I_2(s) + 2\,OH^-(aq) + 3\,H_2O\,(\ell)$

(c) $Pb^{2+}(aq) + O_3(g) + H_2O(\ell) \rightleftharpoons PbO_2(s) + O_2(g) + 2\,H^+\,(aq)$

Answer: 8.56×10^9, 1.0×10^{193}, 5.98×10^{20}

3. The osmotic pressure of H_2SO_4 solution is 1283 kPa at 380 K. Calculate molarity of a solution. Assume 100 per cent ionization of sulfuric acid.

Answer: 0.135 M

16.8 d-Block elements

GENERAL FEATURES OF THE D-BLOCK ELEMENTS

The d-block elements have a general electronic configuration $\mathbf{ns^2(n-1)d^x}$, where ***x*** is a number of electrons in a d-subshell. It takes the numerical values from one to ten. Only some elements (for example, Cu, Ag, Au, Cr and Mo) exhibit configuration $\mathbf{ns^1(n-1)d^x}$, where ***x*** equals to 5 or to 10.

The d-block elements fall in the periodic table between the s-block and the p-block elements. They are often called the *transition elements* or *transition metals*. Their properties are intermediate between s-block elements and p-block elements. They are more electropositive than p-block elements but less electropositive than s-block elements.

Transition metals are strictly defined as elements with one or more stable ions which have incompletely filled d-orbitals. In their atoms there are five separate d-orbitals each of which can accommodate two electrons of opposite spin. These five orbitals 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 electronic configurations of the atoms with electronic configuration $\mathbf{ns^1(n-1)d^x}$. For example, for chromium and copper they are respectively $3d^54s^1$ and $3d^{10}4s^1$. It also explains why Fe^{2+} cations ($3d^6$) are easily oxidized to Fe^{3+} ($3d^5$), but Mn^{2+} ($3d^5$) is not readily oxidized to Mn^{3+} ($3d^4$).

The peculiarity of d-block elements is the lack of monotonic alteration in their atomic radii in periods and groups (table 16.18). Moving along the period, we notice first decrease in atomic radii, and then a slight increase in their numerical values. The alteration of atomic radii across the period from Sc to Zn is represented in figure 16.3.

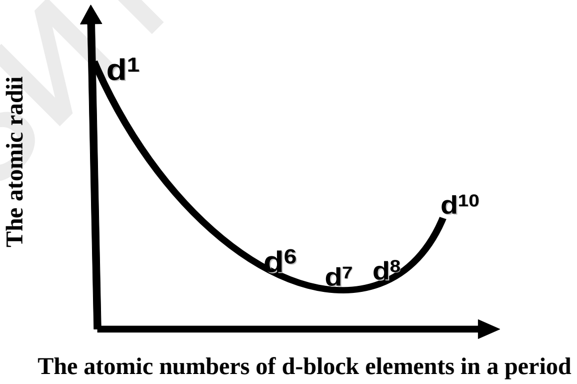


Figure 16.3 — The alteration of atomic radii across the period from Sc to Zn

The same trend is observed in the horizontal change of ionization energy, electron affinity and electronegativity of atoms. *The effect of d-compression* is responsible for this phenomenon. The effect of d-compression is defined as *the penetration of valence d-electrons to nuclei that causes decrease in atomic radii.* For the elements with d^1, d^2 and d^3 electronic configurations d-compression is highly expressed, but for d^9 and d^{10} configurations — it is negligibly low.

Table 16.18 — Physiochemical properties of the d-block elements from Sc to Zn

Element	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Electronic configuration	[Ar] $3d^{1}4s^{2}$	[Ar] $3d^{2}4s^{2}$	[Ar] $3d^{3}4s^{2}$	[Ar] $3d^{5}4s^{1}$	[Ar] $3d^{5}4s^{2}$	[Ar] $3d^{6}4s^{2}$	[Ar] $3d^{7}4s^{2}$	[Ar] $3d^{8}4s^{2}$	[Ar] $3d^{10}4s^{1}$	[Ar] $3d^{10}4s^{2}$
Atomic Radii, nm	0.164	0.146	0.134	0.127	0.130	0.126	0.125	0.124	0.128	0.139
Ionization Potential, eV	6.56	6.82	6.74	6.77	7.43	7.89	7.87	7.63	7.73	9.39
Electro Negativity	1.20	1.32	1.45	1.56	1.60	1.64	1.70	1.74	1.75	1.66

The effect of d-compression is responsible for the formation d-block elements triads located in GroupVIIIB. Three elements of the fourth period (iron, cobalt and nickel) form *iron triad*, and the rest elements of GroupVIIIB (ruthenium, rhodium, palladium, osmium, iridium, and platinum) form the triads of platinum metals. The triad elements are not electronic analogues but they exhibit similar physiochemical properties due to close values of their atomic radii and other atomic characteristics.

The metallic properties of transition metals show no regularity in their changing in groups from top to bottom. Analyzing the data of table 16.19, we can see the general tendency in changing ionization potentials of atoms in groups. From top to bottom they are slightly increased, but in groups IIB, VIB and VIIB the ionization potential of the second element is less than that of the first and greater than that of the third. Thus, the metallicity of d-block elements in groups tends to decrease from top to bottom that distinguishes them from s- and p-block elements.

Table 16.19 — Changing of ionization potentials in the groups of transition metals

IB		**IIB**		**VIB**		**VIIB**	
Element	**Ionization potential, eV**	**Element**	**Ionization potential, eV**	**Element**	**Ionization potential, eV**	**Element**	**Ionization potential, eV**
Cu	7.33	Zn	9.39	Cr	6.77	Mn	7.43
Ag	7.58	Cd	8.99	Mo	7.10	Te	7.28
Au	9.23	Hg	10.4	W	7.98	Re	7.88

Attention ought to be drawn to the fact that the physiochemical properties of the d-block elements vary in the periods and in the groups not so rapidly as they do in s- and p-block elements. This is because in the transition metals, although the nuclear charge is increasing in periods by one, an electron is added to an inner d-orbital. In the second period from Li to F a valence electron is added, that’s why their properties vary rapidly. But when an electron is added to an inner orbital, the difference from element to element is only small.

The certain characteristic property of transition elements is their variable oxidation states in compounds. The reason for variable oxidation state is that there is a very small energy difference between **(n-1)d** and **ns** orbitals. As a result, electrons of (n-1) d orbitals as well as ns-orbitals take part in bond formation. Variation in oxidation state is related to their electronic configuration. Table 16.20

summarizes the possible oxidation states of the first row of transition metals. Common oxidation states are in bold print.

Table 16.20 — Variable oxidation states of d-block elements

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					

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 and their ions are therefore easily oxidized and reduced and are involved in numerous oxidation-reduction reactions. They 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.

d-Block elements are the best complexing agents, as they are characterized by small ionic radii and relatively high oxidation states. The elements of triads are the most powerful complexing agents, because due to the effect of d-compression they exhibit the smallest ionic radii in a period. This statement gives reason why d-block elements present in biological systems only in the form of complex compounds with bioligands.

The most important compounds of d-block elements include *oxides, hydroxides* and *hydrides.* Their oxides and hydroxides may be basic, acidic or amphoteric. It is interesting to note that acidity and basicity of these compounds depend upon oxidation state of the element. The greater the oxidations state of an element, the greater the acidity of its oxides and hydroxides (table 16.21).

Table 16.21 — The effect of oxidation states at the character of oxides and hydroxides of iron, copper and manganese

Element	**Oxidation state**	**Oxides and hydroxides**	**Types of compounds**
Fe	+2	FeO, $Fe(OH)_2$	Basic
	+3	Fe_2O_3, $Fe(OH)_3$	Slightly amphoteric
	+6	FeO_3, H_2FeO_4	Acidic
Cr	+2	CrO, $Cr(OH)_2$	Basic
	+3	Cr_2O_3, $Cr(OH)_3$	Amphoteric
	+6	CrO_3, H_2CrO_4	Acidic
Mn	+2	MnO, $Mn(OH)_2$	Basic
	+3	Mn_2O_3, $Mn(OH)_3$	Basic
	+4	MnO_2, $MnO(OH)_2$	Amphoteric
	+6	MnO_3, H_2MnO_4	Acidic
	+7	Mn_2O_7, $HMnO_4$	Acidic

Most d-block elements react with hydrogen with the formation of metallic hydrides that are electrically conducting solids. The hydrides are the compounds of variable composition, e.g. $TiH_{1.7}$ or $TiH_{0.9}$. Platinum metals form solid solutions with hydrogen.

Manganese, iron, cobalt, copper, zinc and molybdenum are d-block elements essential to life. They all are microelements still performing numerous functions in a human body: activate enzymes, are the constituents of hormones and vitamins, and are involved in the processes of blood and tissues respiration.

Cobalt is another element that is necessary for good human health. While cobalt has no specific function by itself, it forms the core of vitamin B-12. Without cobalt, Vitamin B-12 could not exist. The body uses this vitamin for numerous of purposes. B-12 is necessary for the normal formation of all cells, especially red blood cells. Vitamin B-12 also helps vitamin C perform its functions, and is necessary for the proper digestion of the food that we eat. Additionally, vitamin B-12 prevents nerve damage by contributing to the formation of the protective sheath that insulates nerve cells. A deficiency of vitamin B-12 can cause our red blood cells to form improperly. This can prevent our red blood cells from carrying enough oxygen from our lungs to the different parts of our bodies, thus causing a condition called anemia. Symptoms of anemia include loss of energy, loss of appetite, and moodiness. B-12 deficiency can also cause nerve cells to form incorrectly, resulting in irreversible nerve damage. This situation is characterized by symptoms such as delusions, eye disorders, dizziness, confusion and memory loss. Unlike other B complex vitamins, vitamin B-12 can be stored in the body. Because of this, it is very easy to get enough of this important vitamin in your diet. Deficiencies of B-12 are rare in young people, but do occasionally occur in adults due to digestive disorders or poor absorption by the digestive system. Strict vegetarians are also at risk of B-12 deficiency, because vegetables do not contain this important vitamin. B-12 is only found in animal sources such as red meat, fish, eggs, cheese and milk. Fortunately for vegetarians, you can also get plenty of vitamin B-12 from most multi-vitamin pills.

Copper is an essential micro element that is required for plant, animal, and human health. In its many forms, copper is the third most common mineral in the body. In addition to being important for many enzyme systems, copper is found throughout the muscular-skeletal system, although the largest amounts are found in the brain and liver. Copper, through its involvement in the formation of several key enzymes is not only involved in the release of energy inside the cell, but also contributes to the function of very many antioxidants, assisting the «mopping up» of the free radicals that cause cell damage. The formation and regulation of hormones such as melatonin is under the control of copper, via its role in the blood protein ceruloplasmin and copper enzymes are also responsible for the production of a wide range of neurotransmitters and other neuroactive compounds, including the catecholamines and encephalins. Collagen production, formation of red blood cells and the oxidation of fatty acids are all highly dependent on copper concentration. Thankfully, copper deficiency is rare. However, due to the intricate interaction with zinc (copper and zinc compete for the same absorption sites in the gut), high zinc levels can prevent proper absorption. Copper's essentiality was first discovered in 1928, when it was demonstrated that rats fed a copper-deficient milk diet were unable to produce sufficient red blood cells. The anemia was corrected by the addition of copper-containing ash from vegetable or animal sources.

Iron is an essential element for most life on Earth, including human beings. It is needed for a number of highly complex processes that continuously take place on a molecular level and that are indispensable to human life, e. g. the transportation of oxygen around your body. Iron is required for the production of red blood cells but it's also part of hemoglobin binding to the oxygen and thus facilitating its transport from the lungs via the arteries to all cells throughout the body. Once the oxygen is delivered the iron (as part of hemoglobin) binds the carbon dioxide which is then transported back to the lung from where it gets exhaled. Iron is also involved in the conversion of blood sugar to energy. Metabolic energy is crucial for athletes since it allows muscles to work at their optimum during exercise or when competing. The production of enzymes (which play a vital role in the production of new cells, amino acids, hormones and neurotransmitters) also depends on iron, this aspect becomes crucial during the recovery process from illnesses or following strenuous exercise or comprting. The immune system is dependent on iron for its efficient functioning and physical and mental growth require sufficient iron levels, particularly important in childhood and pregnancy, where the developing baby solely depends on its mother's iron supplies. Iron is lost by the body through a variety of ways including urination, defecation, sweating, and exfoliating of old skin cells. Bleeding contributes to further loss of iron which is why women have a higher demand for iron than men. If iron stores are low, normal hemoglobin production slows down, which means the transport of oxygen is diminished, resulting in symptoms such as fatigue, dizziness, lowered immunity or reduced sports performance in athletes. Since our bodies can't produce iron itself we need to make sure we consume sufficient amounts of iron as part of our daily diet.

Manganese is actually an extremely important element that the body uses for a variety of things. It supports the immune system, regulates blood sugar levels, and is involved in the production of energy and cell reproduction. This element is also important for bone growth. Additionally, manganese works with vitamin K to support blood clotting. Working with the B-complex vitamins, manganese helps to control the effects of stress while contributing to ones sense of well being. Though it is extremely rare in humans, it is suspected that not getting enough manganese can cause poor bone formation, affect our fertility and the ability for our blood to clot. Birth defects can possibly even result when an expecting mother doesn't get enough of this very important element. Some researchers are also looking into a link between poor manganese intake and higher skin cancer rates. The fact that manganese is so important to humans, yet deficiencies in humans are so rare, may indicate that humans have evolved ways to make sure that we don’t ever run out of this element in our bodies. As is the case with most, if not all, elements, we can easily get enough manganese from a good balanced diet. Foods high in manganese include avocados, berries, nuts and seeds, egg yolks, whole grains, green leafy vegetables and legumes (such as peanuts, peas and beans).

Molybdenum is a microelement necessary for good health, though in extremely small amounts. Molybdenum is found in all tissues of the human body, but tends to be the most concentrated in the liver, kidneys, skin and bones. It is required for the proper function of several biochemical reactions in the human body. Some of these reactions have the very important job of allowing the body to process the iron and nitrogen in our diets. Molybdenum is believed to be important in helping our cells grow. Also, small amounts of dietary molybdenum have been credited with promoting healthy teeth. Some evidence suggests that molybdenum might reduce the risk of some types of asthma attacks. A deficiency of molybdenum in our diets can cause mouth and gum disorders and can contribute to getting cancer. A diet high in refined and processed foods can lead to a deficiency of molybdenum, resulting in anemia (lack of oxygen in the blood), loss of appetite and weight, and stunted growth in animals. The amount of molybdenum in plant foods varies significantly and is dependent upon the mineral content of the soil that the plants were grown in. Nevertheless, the best sources of this mineral are beans, legumes (peanuts and peas), dark green leafy vegetables, and grains. Hard tap water can also supply molybdenum to the diet.

Zinc is an important trace mineral that people need to stay healthy. This element is second only to iron in its concentration in the body. Zinc is found in cells throughout the body. It is needed for the body's defensive (immune) system to properly work. It plays a role in cell division, cell growth, wound healing, and the breakdown of carbohydrates. Zinc is also needed for the senses of smell and taste. During pregnancy, infancy, and childhood the body needs zinc to grow and develop properly. Recent information from an expert review on zinc supplements showed that:

- when taken for at least 5 months, zinc may reduce your risk of becoming sick with the common cold;
- starting to take zinc supplements within 24 hours after cold symptoms begin may reduce how long the symptoms last and make the symptoms less severe.

High-protein foods contain high amounts of zinc. Beef, pork, and lamb contain more zinc than fish. The dark meat of a chicken has more zinc than the light meat. Other good sources of zinc are nuts, whole grains, legumes, and yeast. Fruits and vegetables are not good sources, because the zinc in plant proteins is not as available for use by the body as the zinc from animal proteins. Therefore, low-protein diets and vegetarian diets tend to be low in zinc. Zinc is in most multivitamin and mineral supplements. These supplements may contain zinc gluconate, zinc sulfate, or zinc acetate. It is not clear whether one form is better than the others. Symptoms of zinc deficiency include (a) frequent infections, (b) hypogonadism in males, (c) loss of hair, (d) poor appetite, (e) trouble seeing in the dark, (f) wounds that take a long time to heal.

The brief data about content of d-block elements in a human body and their biological functions are given in Appendix Table 9.

16.9. Laboratory work

QUALITATIVE REACTIONS ON THE CATIONS OF d-BLOCK METALS

TEST 1. Qualitative reactions on Cu^{2+}

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?

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

Add 3–5 drops of of NH_4OH solution. What can you see?

$$(CuOH)_2SO_4 + (NH_4)_2SO_4 + 6\ NH_4OH \rightarrow 2\ [Cu(NH_3)_4]SO_4 + 8\ H_2O$$

TEST 2. Qualitative reactions on Ag^{+}

Pour 2–3 drops of $AgNO_3$ 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?

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

Add 2–3 drops of HNO_3 solution into a test tube. What can you see?

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

TEST 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?

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

Separate the prepared 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?

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

2. Pour 3–5 drops of any Zn^{2+} salt solution into a test tube and add 2–3 drops of $K_4[Fe(CN)_6]$ solution. What can you see?

$$3\ ZnCl_2 + 2\ K_4\ [Fe\ (CN)_6] \rightarrow K_2Zn_3\ [Fe\ (CN)_6]\downarrow + 6\ KCl$$

TEST 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.

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

Warning! All forms of mercury are toxic. Doing experiments with solutions of mercury salts you must avoid their contact with skin.

TEST 5. Qualitative reactions on Cr^{3+}

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

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

Separate the prepared 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?

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

2. Pour 2–3 drops 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_2O_2 solution. What can you see?

$$Na_3[Cr(OH)_6] + H_2O_2 \rightarrow Na_2CrO_4 + NaOH + H_2O$$

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

TEST 6. Qualitative reactions on Mn^{2+}

1. Pour 3–5 drops 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_3 solution into a test tube and add 2–3 drops of any Mn^{2+} salt. Mix the solutions and add some crystals of $NaBiO_3$.What can you see?

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

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

TEST 7. Qualitative reactions on Fe^{2+}

1. Prepare a solution of $FeSO_4$ salt. Pour 2–3 drops of a prepared solution into a test tube and add 2–3 drops of $K_3[Fe(CN)_6]$. What can you see?

$$FeCl_2 + K_3[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6]\downarrow + 2\,KCl$$

2. Pour 3–5 drops of $FeSO_4$ 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?

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

TEST 8. Qualitative reactions on Fe^{3+}

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

$$FeCl_3 + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6]\downarrow + 3\,KCl$$

2. Pour 3–5 drops 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 9. Qualitative reactions on Co^{2+}

1. Pour 3–5 drops 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 Co^{2+}salt solution into a test tube and add 8–10 drops of saturated NH_4CNS solution. What can you see?

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

TEST 10. Qualitative reactions on Ni^{2+}

Pour 3–5 drops 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 prepared precipitate in ammonia solution:

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

16.10. Problems

DISCUSSION QUESTIONS

1. Write the electronic configurations for the following atoms and ions:

(a) Cu (b) Fe^{2+} (c) Zn^{2+} (d) Fe^{3+} (e) Cr (f) Co^{2+}

2. Complete the following reduction-oxidation reactions and balance them using half-reaction method:

(a) $K_2Cr_2O_7 + NaBr + H_2SO_4 \rightarrow$
(b) $Cr_2(SO_4)_3 + H_2O_2 + KOH \rightarrow$
(c) $KMпO_4 + KNO_2 + KOH \rightarrow$
(d) $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \rightarrow$
(e) $K_2Cr_2O_7 + KI + HCI \rightarrow$

3. Write reactions for the following salts hydrolysis:

(a) $FeCl_3$ (b) $Zn(NO_3)_2$

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

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

5. Use table 16.8 «Presentation of an element» to describe bioessential metals iron and copper.

6. Explain, how acid-base properties of hydroxides changes in a series:

$$Cr(OH)_2 \rightarrow Cr(OH)_3 \rightarrow H_2CrO_4.$$

Prove your conclusions with the help of chemical reactions.

7. Complete the equations of the following complex-formation reactions:

(a) $AgCl + NH_3$ (excess) $\rightarrow$ (b) $Co\ (NO_3)_2 + NH_4CNS$ (excess) $\rightarrow$
(c) $Fe\ (CN)_3 + KCN$ (excess) $\rightarrow$ (d) $HgI_2 + KI$ (excess) $\rightarrow$

Give systematic names for the prepared complex compounds.

NUMERICAL EXERCISES

1. Calculate molarity of silver cations Ag^+ in saturated solutions of the following salts:

(a) $AgCl$ ($K_{sp} = 1.78\times10^{-10}$); (b) Ag_2S ($K_{sp} = 6.3\times10^{-50}$), and
(c) Ag_3PO_4 ($K_{sp} = 1.3\times10^{-20}$).

Answer: (a) 1.33×10^{-5} M, (b) 2.51×10^{-8} M, (c) 4.68×10^{-6} M

2. Calculate the emf of the following concentration cell at 298 K:
$Zn\ (s)\ /\ Zn^{2+}$ (0.25 M) // Zn^{2+} (0.50) M) / Zn (s).

Answer: 8.9 mV

3. The formation constant of complex anion $[HgI_4]^{2-}$ is 2.0×10^{30}. Calculate molarity of Hg^{2+} cations in 0.5 M $K_2[HgI_4]$ solution.

Answer: 2.5×10^{-7}M

CHAPTER 17
SURFACE PHENOMENA. ADSORPTION

United we stand

After reading this chapter, you should be able to:

- explain the origin of free surface energy accumulated in the interface monolayer;
- define adsorption and its types;
- discuss structure and special properties of surfactants; give mathematical description for their adsorption at liquid-gas interface surface;
- describe molecular adsorption on solid sorbents; discuss the Langmuir, the BET and the Freundlich isotherms;
- describe selective and ion exchange adsorption of electrolytes from aqueous solutions on solid adsorbents;
- define chromatography and classification of chromatographic methods.

17.1. Surface phenomena and surface tension

A thin monomolecular layer situated at the boundary of two different phases accumulates a huge amount of free surface energy (G_s). This energy promotes a number of processes defined as **surface phenomena**. **Surface phenomena are those processes, which run spontaneously at the interface surfaces.** They are: adhesion, cohesion, adsorption, absorption and some others. Such phenomena play an essential role in metabolic processes such as respiration, digestion, and excretion. These processes run *in vivo* at highly developed interface surfaces. For example, skin surface is approximately 1.5 m^2, erythrocytes surface is 3,000 m^2 and alveoli surface — 1,000 m^2.

Accumulation of free energy at the interface surface is a result of non-balanced intermolecular forces affecting a molecule at a surface. Let's consider the energy state of molecules in a single component system composed of two phases: liquid water – water vapor. A molecule in the interior is completely surrounded by other molecules each of which exerts attractive forces (f_1). These forces are mutually balanced: $\Sigma f_1 = 0$ (figure 17.1).

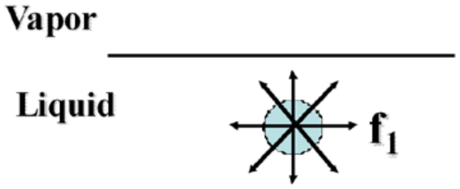


Figure 17.1 — A molecule in the interior of a liquid phase

A molecule at a surface has other molecules beside it and beneath it but only few molecules above it: $f_2 << f_1$, where f_2 is an intermolecular force in vapor. As a result, the net intermolecular force f_3 pulls the molecules towards the interior of the liquid (figure 17.2).

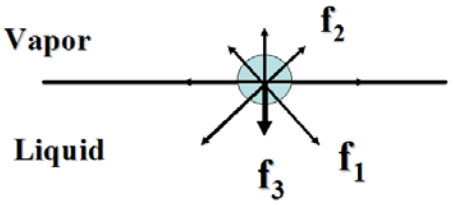


Figure 17.2 — A molecule at a liquid surface

The net intermolecular force is responsible for intermolecular pressure of liquids, which is rather high. For water it is equal to 14 000 atm /cm^2. Intermolecular pressure makes liquids incompressible. Non-balanced intermolecular forces effecting molecules at the surface are responsible for their high potential energy in comparison with molecules in the interior. The difference between energies of surface molecules and molecules in the interior is defined as free surface energy:

$$G_s = \sigma \times S \qquad (17.1)$$

where S is the area of interface surface, m^2;

σ — proportionality coefficient, named surface tension, $\frac{k\ J}{m\ \ o}$ or $\frac{N}{ml}$

From equation 17.1 we can derive that:

$$\sigma = \frac{G_s}{S}, \qquad (17.2)$$

Thus **surface tension is the amount of free surface energy per area unit**. The factors effecting surface tension of liquids are: (a) temperature, and (b) polarity of medium. Temperature elevation gives decrease in surface tension since results in some intermolecular bonds' cleavage. The greater is polarity of a liquid the greater is its surface tension since increase in polarity gives increase in intermolecular forces (table 17.1).

Surface tension is an important characteristic of liquids, solutions and biological fluids. For example, surface tension of blood is 45.4×10^{-3} N/m. Even negligible deviation from a normal value signals about serious diseases. Stalogmometric method is wide applied in practice to measure surface tension of liquids.

According to the Second Law of chemical thermodynamics free surface energy tends to zero ($G_s \rightarrow 0$). This tendency is carried out by: (a) decrease in interface surface area (confluence of drops, liquids aspiration for a shape of sphere, because a sphere has the smallest possible surface area to volume ratio.), (b) another way to diminish G_s is adsorption.

Table 17.1 — Surface tension of some liquids at 298 K

Liquids	**Dielectric constant, ε**	**σ × 10^3, N/m**
Sulfuric acid H_2SO_4	101	476
Water	78.5	72.7
Ethyl alcohol C_2H_5OH	24.3	22.3
Hexane C_6H_{14}	1.89	18.4

17.2. Adsorption and its types

Adsorption is the attachment of particles of adsorbates to the surface of adsorbents. The process of adsorption involves separation of substances from one phase accompanied by its accumulation at the surface of another (figure 17.3).

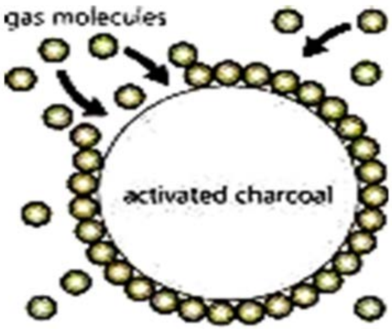


Figure 17.3 — Adsorption of gas molecules at the surface of activated charcoal

When we discuss such a phenomenon as **sorption,** it is necessary to distinguish between adsorption and absorption. **Absorption** is a physiochemical process in which atoms molecules, or ions enter some bulk phase — gas, liquid, or solid material. This is a different process from adsorption since molecules undergoing absorption are taken up by the volume, not by the surface (figure 17.4).


Absorbtion Adsorbtion

Figure 17.4 — We must distinguish between adsorption and absorption

The adsorbing phase is the **adsorbent,** and the material concentrated at the surface of that phase is the **adsorbate.** Adsorbed amount (Γ) is defined as:

$$\Gamma = \frac{\nu}{s} \tag{17.3}$$

where **ν** is an amount of an adsorbate, mol;

S is an area of an interface surface, m^2;

Adsorbed amount (**Γ**) is expressed in mol/m^2.

Molecules and atoms can attach to surfaces in two different ways**. In physical adsorption** there is a van der Waals interaction between adsorbents and adsorbates. Such an interaction is weak and adsorption is reversible. Energy of physical adsorption is rather low: approximately 4–40 kJ/mol. **In chemical adsorption (chemisorption)** the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond. Chemisorption is an irreversible process. Its energy is approximately 40–400 kJ/mol.

Adsorption may occur at the different interface surfaces: (a) liquid / gas, (b) liquid / liquid, (c) solid / liquid, and (d) solid / gas.

17.3. Surfactants adsorption at gas / liquid interface surfaces

When substances are dissolved in water its surface tension may be increased, decreased, or doesn't alter (figure 17.5).

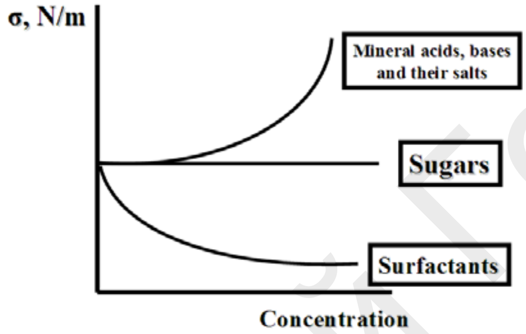


Figure 17.5 —Isotherms of surface tension

Surfactants or surface-active agents are substances that reduce surface tension of water. Surfactants are dual — nature molecules consisting of polar hydrophilic head group and non-polar hydrocarbon tail or radical (figure 17.6):

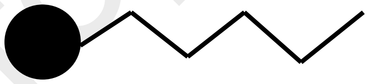


Figure 17.6 — A scheme of surfactant molecule

Surfactants fall into two categories: (a) electrolytes and (b) non electrolytes.

Surfactants-electrolytes are subdivided into two groups: *cationic* and *anionic*. The bright examples of cationic surfactants are salts and hydroxides of alkyl ammonium.

For example, cetyl trimethyl ammonium bromide $[CH_3\text{-} (CH_2)_{15}N\ (CH_3)_3]Br$ is applied as antiseptic in surgery. Anionic surfactants are salts of carboxylic acids (R-COOMe) and salts of sulphonic acids ($R\text{-}SO_3Me$).

Surfactants – weak or non electrolytes are abundant in nature. They are:

- carboxylic acidsR–COOH;
- sulphonic acids$R–SO_3H$;
- alcoholsR–OH;
- thiolsR–SH;
- amines$R–NH_2$.

Many bioactive substances exhibit surface activity. They are phospholipids, bile salts, amino acids and proteins. Their surface activity is responsible for their biological activity. Phospholipids are the structural components of cell membranes (figure 17.7). Bile acids and their salts are powerful surface active agents needed to aid in the digestion of lipids and in the absorption of vitamins A, D, E, and K from the intestinal tract.

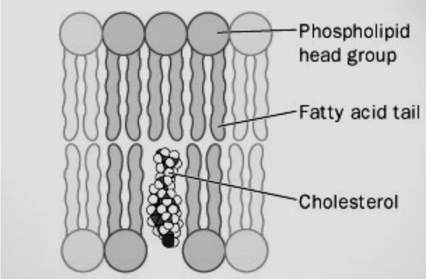


Figure 17.7. — A structure of cell membranes

Adsorption of surfactants at gas / liquid interface surfaces obeys the rule: «Like dissolves like». Their polar hydrophilic head groups tend to be in water while non-polar hydrocarbon tails try to be in air (figure 17.8).

(a) **(b)**

Figure 17.8 — Surfactants adsorption at the liquid-gas interface surface: (a) unsaturated monolayer, (b) saturated monolayer

Surfactants reduce surface tension of water because they change the structure of interface surface and decrease polarity of a medium. The effect of surfactant's concentration at their adsorbed amount from water solutions is represented in a graph form. This graph representation is defined as isotherm of surfactants adsorption (figure 17.9). In dilute solutions increase in surfactants' concentration gives increase in adsorbed amount but adsorbed amount doesn't alter when a saturated monolayer is formed. Maximum adsorbed amount Γ_{max} corresponds to a saturated monolayer.

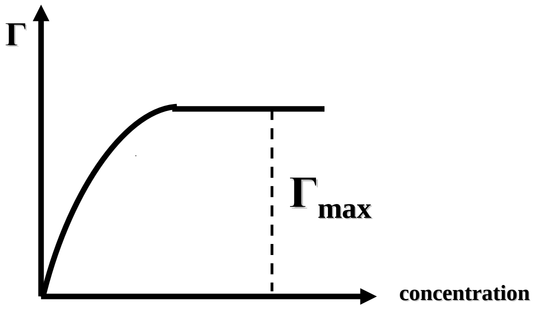


Figure 17.9 — Isotherm of surfactants adsorption

It is possible to calculate a length of a surfactant' molecule (ℓ) and an area occupied by it at interface surface (s) when maximum adsorbed amount is determined. A length of a surfactant' molecule (ℓ) is:

$$\ell = \frac{\Gamma_{\max} \times M}{\rho} \qquad (17.4)$$

where ρ is a density of a surfactant;
M is it's molar mass.

An area occupied by a molecule at interface surface (s) can be calculated according to the equation:

$$S = \frac{1}{\Gamma_{\max} \times N_A}, \qquad (17.5)$$

where N_A is the Avogadro number.

Surfactants are characterized by their surface activity (g):

$$g = -\frac{\Delta\sigma}{\Delta C} \qquad (17.6)$$

where Δσ is a decrease in surface tension which corresponds to increase in surfactant's concentration by ΔC.

Surface activity of substances depends upon their nature. This dependence is expressed by the empiric **Traube's Rule (**1884): **the surface tension of the organic compounds belonging to the homological series of $R(CH_2)n$ X shows certain regularity. For each additional CH_2 group the surface activity is increased by factor 3–3.5.**

Illustration of the rule is given in figure 17.10.

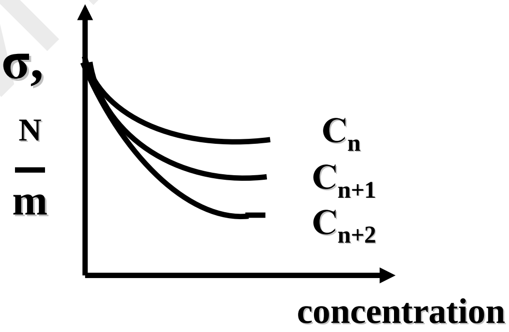


Figure 17.10 — The family of isotherms of surface tension

The relationship between adsorbed amount (Γ) and surfactants' concentration in water solution at a constant temperature is expressed by **the Gibbs's equation** (1878):

$$\Gamma = -\frac{d\sigma}{dC} \times \frac{C(sur)}{RT}, \qquad (17.7)$$

where C is a concentration of a surfactant, moℓ/ℓ;
R is a gas constant, 8.31 J/moℓ×K;
T — absolute temperature, K.

The effect of surfactants on surface tension of solutions is expressed by **the Shishkovsky's equation** (1909):

$$\sigma = \sigma_o - a \times \ell n\ (1 + b \times c), \qquad (17.8)$$

where **a** and **b** are the parameters of the Shishkovsky's equation.

The adsorbed amount may be calculated by the combined **Gibbs-Shishkovsky's equation:**

$$\Gamma = \frac{a}{RT} \times \frac{bC_M}{1 + bC_M}, \qquad (17.9)$$

EXAMPLE 17.1. The relationship between a surface tension of butyric acid solution and its concentration at 20 °C is described by the Shishkovsky's equation:

$$\sigma = \sigma_o - 29.8 \times 10^{-3} \times \ln (1 + 19.64 \times C).$$

Calculate the butyric acid adsorbed amount when $C_M = 0.01$ mol/ℓ.

ANSWER. The adsorbed amount of butyric acid can be calculated according to the equation 17.9:

$$\Gamma = \frac{29.8 \times 10^{-3}}{8.31 \times 293} \times \frac{19.64 \times 0.01}{1 + 19.64 \times 0.01} = 2 \times 10^{-6}\,\text{mol/m}^2$$

Surfactants are wide applied in different areas of people activity. In everyday life they are used as soaps and detergents. They remove water-insoluble grease (e. g. butter, fat and oil) from solid surfaces. Their cleaning effect is based on the fact that the surfactant molecules adsorb on the contaminated surfaces, turning hydrophobic to hydrophilic systems (figure 17.11). Such hydrophilic systems are soluble in water and are readily swept away, leaving clean surfaces behind.

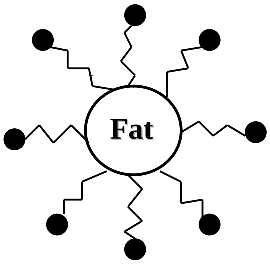


Figure 17.11 — The hydrophobic system turned to become hydrophilic (soluble in water)

In modern medicine some surfactants are applied as antiseptics in surgery. Their antibacterial activity is much greater (~300 times) than that of phenol traditionally applied in medicine for disinfection. Surfactants affect permeability of microorganisms' cell membranes and inhibit their enzyme systems.

Surfactants are used for liposome (from Greek «lipos» — fat, «soma» — body) productions. **Liposome** — is a super molecular structure composed of phospholipids bilayer and an interior solution (figure 17.12).

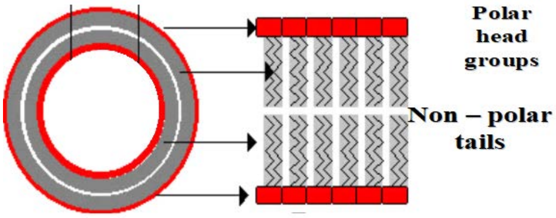


Figure 17.12 — Liposome structure

An interior solution can contain any medicine which is transported to the certain organ or tissue, which has affinity to the phospholipids a liposome is composed from. Liposomes may be used to carry a wide range of medicines in blood (antitumor and antibacterial drugs, hormones and vaccines).

17.4. Solid adsorbents and their classification

Solid sorbents are natural or artificial substances with highly developed surface area. Porous and powered substances have a higher adsorption capacity than nonporous. Sorbents are characterized by their *specific surface area* (a_s):

$$a_s = \frac{A_s}{m}, \qquad (17.10)$$

where A_s is the surface area of the solid sorbent, m^2;
m — mass of a sorbent, g.
For example, specific surface area of activated carbon is equal to 1×10^3 m^2/g.

Classification of solid sorbents

1. Carbonaceous sorbents (activated carbon is most widely used). **Activated carbon** (figure 17.13) is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. Activated carbon is used for adsorption of organic substances and non-polar adsorbates, and it is also used for waste gas and waste water treatment.

Figure 17.13 — Activated carbon is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder

2. Aluminosilicates are the class of minerals containing aluminum and silicon oxides. For example, kaolin (white clay) $AI_2O_3 \times SiO_2 \times 2\ H_2O$ is an example of wide used solid adsorbents (figure 17.14).

Figure 17.14 — Kaolin (white clay).

3. Zeolites are natural or synthetic crystalline aluminosilicates which have a repeating pore network and release water at high temperature. Zeolites are polar in nature (Figure 17.15). They are manufactured by hydrothermal synthesis of sodium aluminosilicate or another silica source in an autoclave followed by ion exchange with certain cations (Na^+, Li^+, Ca^{2+}, K^+, NH_4^+). Zeolites are applied in drying of process air, CO_2 removal from natural gas, CO removal from reforming gas, air separation, catalytic cracking, and catalytic synthesis and reforming.

Figure 17.15 — Zeolites are natural or synthetic crystalline aluminosilicates that are applied in process of drying air

4. Silica gel is a dehydrated gel of polysilicon acids $(SiO_2)_n$. It is chemically inert, nontoxic, polar and dimensionally stable (figure 17.16). Silica gel is used for drying of process air (e. g. oxygen, natural gas) and adsorption of heavy (polar) hydrocarbons from natural gas.

Figure 17.16 — Silica gel is a dehydrated gel of polysilicon acids $(SiO_2)_n$

5. Oxides and hydroxides of some metals: Al_2O_3, $Al(OH)_3$, Fe_2O_3, $Fe(OH)_3$ and some other. For example, almagel, applied as antacidic drug, contains $Mg(OH)_2$ and $Al(OH)_3$. It provides a long-lasting local neutralization of the gastric juice and reduces the content of hydrochloric acid in it (figure 17.17).

Figure 17.17 — Almagel is applied in medicine as antacidic drug. It contains $Mg(OH)_2$ and $Al(OH)_3$

6. Food fibers (cellulose, pectin and lignin) are essential components of food products. Their main functions in a human body are to activate peristalsis and to remove toxins from an intestinal tract. The daily intake of food fibers ought to be 10–40 grams. Unfortunately in comparison with 1900 their consumption was reduced by 80 %. This has led to deterioration in quality of people life. In Table 17.2 the content of food fibers in some products is represented.

Table 17.2 — The content of food fibers in some products

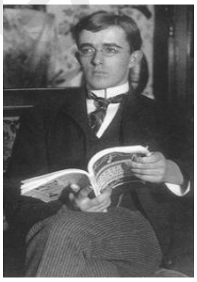
Food products	Grams of food fibers in 100 g of a product
Almond	5.1
Apples	3.9
Maize	3.9
Kidney bean	2.2
Pumpkin	2.2
Cabbage	1.4
Rice	1.3

Three main types of adsorption on solid adsorbents are distinguished:

- molecular adsorption from gaseous and liquid phases;
- selective adsorption of electrolytes from aqueous solutions;
- ion exchange adsorption.

17.5. Molecular adsorption

Molecular adsorption is the adsorption of non electrolytes or weak electrolytes from gaseous and liquid phases. The physical and mathematical explanation for this type of adsorption was started by Langmuir. In 1916 Irving Langmuir published a new model isotherm for gases adsorbed to solids, which retained his name.



Irving Langmuir (1881–1957)

Irving Langmuir was an American chemist and physicist. He investigated electrical discharges in gases, developed a vacuum pump and the high-vacuum tubes used in radio broadcasting. Langmuir formulated theories of atomic structure and chemical bond formation, introducing the term covalence. He received a Nobel Prize in 1932 for his work in surface chemistry.

Langmuir theory is based on the following assumptions.

1. Solid surface is not uniform; its unevenness and roughness act as the active or adsorption sites of the surface.

2. Each adsorption site adsorbs only one adsorbate molecule; all adsorption sites are equivalent:

3. When all adsorption sites are occupied by adsorbate molecules the monolayer is formed. This surface state corresponds to the maximum fractional coverage of a surface. The fractional coverage of a surface(θ) is defined as:

$$\boldsymbol{\Theta} = \frac{\textbf{Number of occupied adsorption sites}}{\textbf{Total number of adsorption sites}}$$

At any temperature the coverage is a function of the applied adsorbate pressure (p) or adsorbate concentration in a liquid phase (c). The variation of θ with gas pressure or concentration at a given temperature is called the Langmuir adsorption isotherm (17.11 and 17.12):

$$\boldsymbol{\Theta} = \frac{\mathbf{K} \times \mathbf{p}}{\mathbf{1} + \mathbf{K} \times \mathbf{p}}, \qquad (17.11)$$

$$\boldsymbol{\Theta} = \frac{\mathbf{K} \times \mathbf{c}}{\mathbf{1} + \mathbf{K} \times \mathbf{c}} \qquad (17.12)$$

where K is an adsorption equilibrium constant which characterizes sorbents selectivity to a particular adsorbate; *p* and *c* are the pressure of the adsorbate and its concentration respectively.

The value of θ in its physical sense is the ratio of the absorbed amount Γ to the maximum Γ_{max}:

$$\boldsymbol{\Theta = \Gamma / \Gamma_{max}} \qquad (17.13)$$

Thus, adsorbed amount of substances from a solution can be calculated by the equation:

$$\boldsymbol{\Gamma} = \boldsymbol{\Gamma}_{\mathbf{max}} \frac{\mathbf{K} \times \mathbf{c}}{\mathbf{1} + \mathbf{K} \times \mathbf{c}} \qquad (17.14)$$

EXAMPLE 17.2. The maximum adsorbed amount of cholesterol on the activated charcoal is 0.7μg/g. How many grams of cholesterol will be absorbed from the plasma on 1 gram of coal? The cholesterol content in plasma is 4.8 μg/ℓ. Assume that adsorption equilibrium constant is 680 μg/ℓ. Cholesterol Molar Mass is 386 g/moℓ.

ANSWER. The adsorbed amount of cholesterol can be calculated according to the equation 17.14:

$$\boldsymbol{\Gamma = 0.7\,\frac{680 \times 4.8}{1 + 680 \times 4.8} = 0.70\ \mu g/g}$$

Mass of adsorbed cholesterol is:

$$\mathbf{m = \Gamma \times M = 0.7 \times 386 = 270\ \mu g\ or\ 2.7 \times 10^{-4}\ g}$$

An assumption of the Langmuir isotherm is the independence and equivalence of the adsorption sites. Deviations from the isotherm can often be traced to the failure of these assumptions. Various attempts have been made to take these deviations into account. The Freundlich isotherm attempts to incorporate the role of substrate-substrate interaction on the surface (figure 17.18):

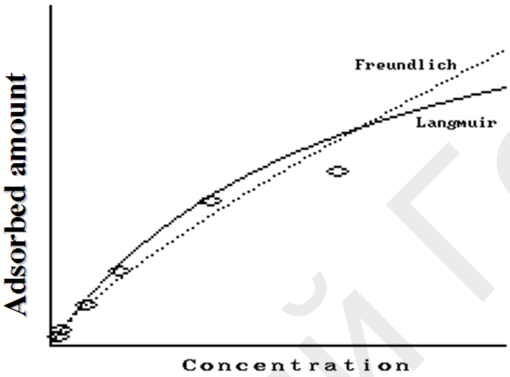


Figure 17.18 — The Freundlich and Langmuir isotherms

The form of Freundlich isotherm is:

$$æ = k \times p^{1/n} \qquad (17.15)$$

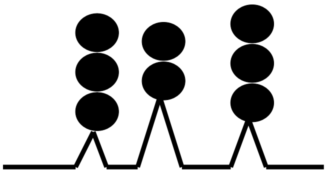
$$æ = k \times c^{1/n} \qquad (17.16)$$

where æ is a mass of an adsorbate on one gram of an adsorbent;

k is the Freundlich equation constant;

n is a parameter of the equation.

The Langmuir isotherm gives a wonderfully simple picture of adsorption at low coverage. At high adsorbate pressures and thus high coverage, this simple isotherm fails to predict experimental results and thus cannot provide a correct explanation of adsorption in these conditions. What is missing in the Langmuir treatment is the possibility of the initial layer of adsorbate to act as a substrate surface itself, allowing for more adsorption beyond saturated (monolayer) coverage.



This possibility has been treated by Brunauer, Emmett, and Teller (1938) and the result is named the **BET isotherm** (figure 17.19).

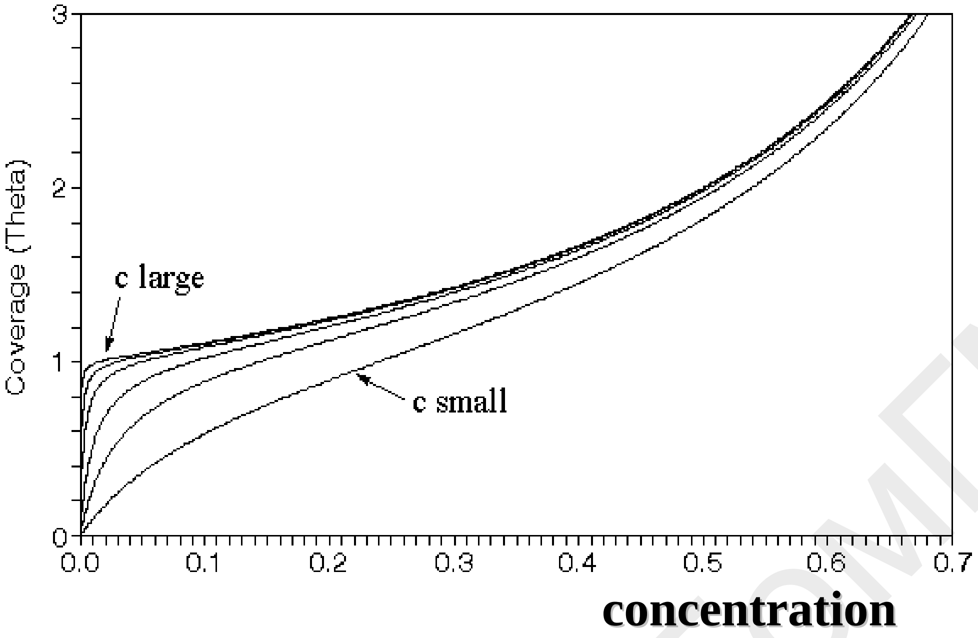


Figure 17.19 — BET isotherm

This isotherm is useful in cases where multilayer adsorption must be considered. The form of this isotherm is:

$$\frac{\mathrm{n}}{\mathrm{n}_{\mathrm{mono}}} = \frac{Cz}{(1-z)[1-z(1-C)]} = (\theta), \qquad (17.17)$$

where n/n_{mono} is the ratio of the moles adsorbed to the moles adsorbed in a single monolayer;

$z = p/p_0$, where p_0 is the vapor pressure of the pure condensed adsorbate.

The n/n_{mono} ratio represents a generalized coverage' because its value can exceed unity. The constant c represents the relative strengths of adsorption and condensation of the pure adsorbate.

17.6. Electrolytes adsorption

The selective adsorption of electrolytes from aqueous solution obeys the **Panet-Phayans' Rules.**

RULE 1. Solid surfaces adsorb those ions that are included into their composition. These ions are defined **as potential determining ions** or **PDI**.

EXAMPLE 17.3. Let us assume that sodium chloride is treated by the excess of silver nitrate solution. The solid surface of silver chloride starts immediately to adsorb ions from a solution. It may adsorb either silver cations Ag^+ or chloride anions Cl^-, but only silver cations are available for adsorption since all chloride anions are precipitated as AgCl. Thus Ag^+ cations behave as potential determining ions, giving positive charge to the solid surface (figure 17.20):

$$\underset{\text{excess}}{AgNO_3} + NaCl \rightarrow AgCl\ (s) + NaNO_3$$

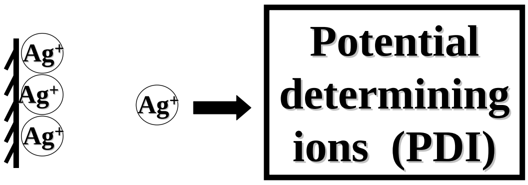


Figure 17.20 — Formation of positively charged PDI layer at the surface of AgCl

EXAMPLE 17.4. When the same chemical process runs with the excess of sodium chloride solution chloride anions Cl^- form a PDI layer at the surface of solid AgCl thus making the surface negatively charged (figure 17.21):

$$AgNO_3 + \underset{\text{excess}}{NaCl} \rightarrow AgCl\ (s) + NaNO_3$$

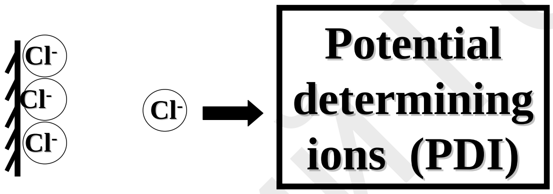
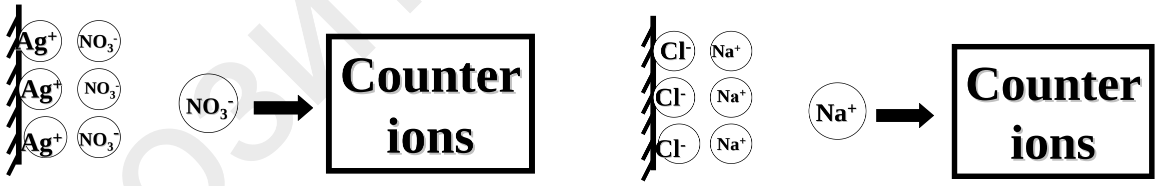


Figure 17.21 — Formation of negatively charged PDI layer at the surface of AgCl

RULE 2. A charged surface adsorbs only oppositely charged ions (**counter ions).** In example 1 positively charged surface adsorbs nitrate anions as counter ions (figure 17.22 a). In the example 17.4 sodium cations operate as counter ions (figure 17.22 b).The electric double layer is formed at the surface of a solid adsorbent:



(a) (b)

Figure 17.22 — The formation of the electric double layer at the surface of AgCl

An ability of ions to be adsorbed on solid surfaces depends upon:

- their electric charge (the greater is a charge, the higher is adsorptivity of ions);
- their ionic radius (the greater is a radius, the higher is adsorptivity of ions).

Ions that carry identical electrical charge but exhibit different adsorptivity are arranged into **lyotropic series**. In these series ions are arranged in the order of an increasing ability to adsorb at the solid surfaces. The greater is an ionic radius of an ion, the stronger is its adsorptivity. The bright examples of lyotropic series are: (a) series of alkali metals cations:

$$\mathbf{Li^+ \quad Na^+ \quad K^+ \quad Rb^+ \quad Cs^+}$$

$$\xrightarrow{\hspace{6cm}}$$

Increase in adsorptivity

(b) series of monoprotic acids anions:

$$\mathbf{Cl^- \quad Br^- \quad NO_3^- \quad I^- \quad CNS^- \quad OH^-}$$

$$\xrightarrow{\hspace{6cm}}$$

Increase in adsorptivity

In the **ion exchange adsorption process** loosely held ions at fixed-charged sites on solids are exchanged with ions that are dissolved in solutions. Solid adsorbents able to take part in ionic exchange are named **ionites** or **ionic exchangers**. There are two types of ionic exchangers: (a) acidic, and (b) basic. Acidic ionites contain loosely held hydrogen cations H^+. Their structure can be represented as $\mathbf{R - H^+}$, where R is a polymer radical.

A great number of solid sorbents operate as acidic ionites. They are aluminosilicates, zeolites, silica gels, cellulose and some other sorbents. Loosely held H^+ cations contained in their crystal lattices undergo reversible exchange with the cations from a solution:

$$\mathbf{R - H^+ + Na^+ \rightleftharpoons R - Na^+ + H^+.}$$

Basic ionites contain loosely held hydroxyl anions OH^-. The examples of them are $Fe(OH)_3$, $Al(OH)_3$ and some other sorbents. Their structure can be represented as:

$\mathbf{R - OH^-}$. They operate according to the scheme:

$$\mathbf{R - OH^- + Cl^- \rightleftharpoons R - Cl^- + OH^-.}$$

Loosely held OH^- anions contained in their crystal lattices undergo reversible exchange with the anions from a solution.

Ionites are applied:

- for purification of drinking and waste waters;
- for blood conservation;
- to test gastric juice acidity;
- for detoxification of a human body.

The tissues of plants and animals are able for ionic exchange. Carboxyl and phosphate groups are responsible for anionic exchange while amino groups are responsible for cationic exchange.

17.7. Adsorption therapy

In modern medicine solid sorbents are applied for: (a) hemo-, lympho– and plasmosorption, (b) enterosorption.

Hemo-, lympho- and plasma-sorption (figure 17.23) are used for blood and other biological fluids purification from toxins by passing of fluids through a column filled with activated carbon or some other sorbents (the method is applied since 60th of 20 century.)

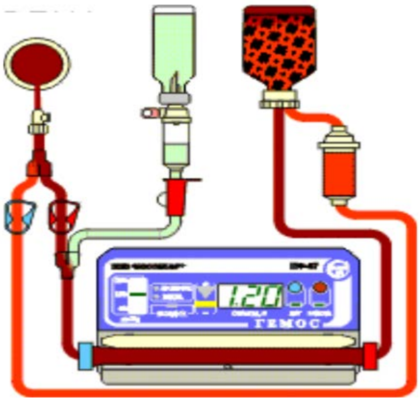


Figure 17.23 — Hemosorption device

Enterosorption is a method to bind and remove toxins in intestinal tract of patients. Enterosorbents are solid sorbents (carbonaceous, aluminosilicates, zeolites and others) that bind and extract toxins, heavy metals, radio nuclides in gastrointestinal tract. Their usage is an affective way to improve the life quality of people living under technogenic pollution in the areas with a high level of chemical and radioactive contamination. The clinic application of hemo- and enterosorbents are:

- at healing of poisoning;
- at complex treatment of liver and kidney disease;
- at treating intestinal infections;
- at healing intestinal infections;
- at treating AIDS.

Professor Jury Lopukhin, who contributed a lot to the development of hemosorption, came to belief that the future will belong to the removing but not to intaking medicine.

17.8. Chromatography

Chromatography is the process of separating the components of mixtures that are distributed between a *stationary phase* and a flowing *mobile phase* according to the rate at which they are transported through the stationary phase.

Chromatography was originally developed by the Russian botanist Michael Tswett in 1903 for the separation of colored plant pigments by percolating petroleum eather extract through a glass column packed with powdered calcium carbonate.

Michael Tswett
(1872–1919)

Michael Tswett is the inventor of the method of chromatographic analysis, acted as the professor of botany and the director of the botanical garden of the Tartu University.

Chromatography is now, in general, the most widely used separation technique in analytical chemistry having developed into a number of related but quite different forms that enable the components of complex mixtures of organic or inorganic components to be separated and quantified. A chromatographic separation involves the placing of a sample onto a liquid or solid *stationary phase* and passing a liquid or gaseous *mobile phase* through or over it, a process known as elution. Sample components, or solutes, whose *distribution ratios* between the two phases differ, will migrate at different rates, and this *differential rate of migration* will lead to their separation over a period of time and distance.

Chromatographic techniques can be classified according to whether the separation takes place on a *planar surface* or in a *column*. They can be further subdivided into *gas* and *liquid chromatography*, and by the physical form, solid or liquid, of the stationary phase and the nature of the interaction of solutes with it, known as *sorption mechanism*. Table 17.3 lists the most important forms of chromatography, each based on different combinations of stationary and mobile phases and instrumental or other requirements.

Paper chromatography (PC) is simple and cheap but lacks the separating power and versatility of *thin-layer chromatography* (TLC) which has largely replaced it. Both require only inexpensive equipment and reagents, and, unlike the various forms of column chromatography, comparisons can be made between a number of samples and standards chromatographed simultaneously. *Gas* and *high-performance liquid chromatography (HPLC)* are complementary techniques best suited to the separation of volatile and nonvolatile mixtures, respectively. Both these techniques are instrumentally-based and computer-controlled, with sophisticated software packages and the ability to separate very complex mixtures of up to 100 or more components. HPLC have several alternative modes suited to different types of solute. For example, *ion-exchange* is a mode that enables mixtures of either anionic or cationic solutes to be separated. *Chiral chromatography* is a mode using for separating mixtures of high molecular mass solutes and enantiomers, respectively.

Table 17.3 — A classification of the principal chromatographic techniques

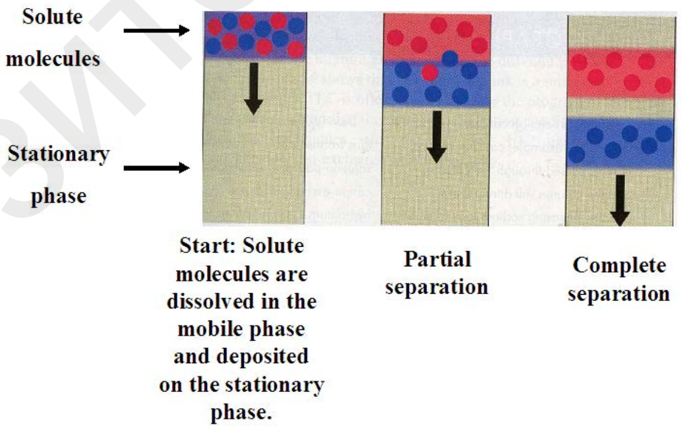
Technique	**Stationary phases**	**Mobile phase**	**Format**	**Principal sorption mechanism**
Paper chromatography	Paper	Liquid	Planar	Partition (adsorption, ion exchange, exclusion)
Thin-layer chromatography	Silica, cellulose, ion-exchange resin	Liquid	Planar	Adsorption (partition, ion-exchange, exclusion)
Gas chromatography				
Gas-liquid	Liquid	Gas	Column	
Gas-solid	Solid	Gas	Column	
				Partition
Liquid chromatography				Adsorption
High-performance liquid chromatography	Solid or bonded-phase	Liquid	Column	Modified partition (adsorption)
Ion-exchange chromatography	Ion-exchange resin	Liquid	Column	Ion-exchange
Chiral chromatography	Solid chiral selector	Liquid	Column	Selective adsorption

The mobile phase dissolves the compounds of interest and carries them over the stationary phase. The rate of movement of compounds depends on how strongly they interact with the stationary phase. Because solutes move only when in the mobile phase, molecules that have a very low affinity for the stationary phase move quickly, whereas those that bind tightly to the stationary phase lag behind. After the materials have traveled a sufficient distance, they become separated into distinct «bands»; each band may contain one pure material. As the mobile phase comes off the lower end of the column, it can be collected in small volumes called *fractions* or *cuts*. When the separations are complete, the various components of the original mixture are found in different fractions.

There are a wide variety of possible uses for chromatography in any area in which you have to identify an unknown substance. In the decades since its invention, the chromatograph has become an essential piece of equipment in bio-chemical laboratories. Using the analytical technique of chromatography, scientists can tell what chemical compounds are present in complex mixtures. These mixtures include such diverse things as smog, cigarette smoke, petroleum products, or even coffee aroma. Without chromatography, chemists might not have been able to synthesize proteins such as insulin or understand how plants use the sun’s energy to make food.

Chemists can use chromatography to analyze drugs and also test blood and urine samples. In drug discovery researches from natural sources, such as plants and animals, crude extracts of specimens containing hundreds of compounds are often used for initial biological screening. Once a hit extract is identified, we need to isolate or separate active principles by using various chromatographic techniques.

In figure 17.24 the diagrammatic view of how column chromatography works is represented.



Start: Solute molecules are dissolved in the mobile phase and deposited on the stationary phase.

Partial separation

Complete separation

Figure 17.24 — The diagrammatic view of how column chromatography works. Solute molecules that bind strongly to the stationary phase move dawn the column more slowly than those that bind only weakly

Toxicology is an area where chromatography is used. Separating and identifying different drugs of abuse. In sports medicine, any illegal drugs will be picked up using chromatographic techniques (for example, gas chromatography).

17.9. Laboratory work surface tension

TEST 1. Studying a relationship between surface tension of solutions and the length of hydrophobic radicals in surfactants

One of the main methods for determining the surface tension of liquids is **stalagmometric method.** Stalagmometer is a capillary tube with an extension of the middle height, ending in thick-walled capillary, through which the liquid is not flowing, but dropping. Above and below the expansion there are the marks A and C (figure 17.25). Stalagmometric method is based on measuring the number of droplets formed by a liquid liberating from the capillary. In this method we compare the number of drops of a test liquid and a number of drops of the liquid with known surface tension (for example, water) falling from the end of a stalagmometer. Surface tension of water is 72.75×10^{-3} N/m at 20 °C.

Figure 17.25 — Stalagmometer is a capillary tube with an extension in the middle

The greater the surface tensions of the liquid, the greater the volume of forming droplets. Thus, the number of droplets is inversely proportional to the surface tension of the liquid:

$$\sigma\,(X) = \sigma(H_2O)\times\frac{n(H_2O)}{n(X)}, \qquad (17.18)$$

where n (H_2O) is a number of water drops and n (X) is a number of drops of a test solution.

Start the experiment with rinsing a stalagmometer with water. Don’t forget that a capillary tube must be scrupulously clean inside. Then fill it with water and calculate the number of water droplets flowing from the capillary between upper mark A and lower mark C. After that rinse the stalagmometer with ethyl alcohol solution (C_2H_5OH) and repeat the experiment. Use the equation 17.18 to calculate the surface tension of the alcohol solution. Repeat the experiment, filling stalagmometer with solutions of propyl (C_3H_7OH), butyl (C_4H_9OH) and amyl ($C_5H_{11}OH$) alcohols respectively. Write the obtained data into the table 17.4.

Table 17.4 — Surface tension of alcohols solutions

N	Alcohols	Number of drops	$\sigma \times 10^3$, N/m
1	H_2O		
2	C_2H_5OH		
3	C_3H_7OH		
4	C_4H_9OH		
5	$C_5H_{11}OH$		

Represent the obtained data in a graph form (figure 17.26).

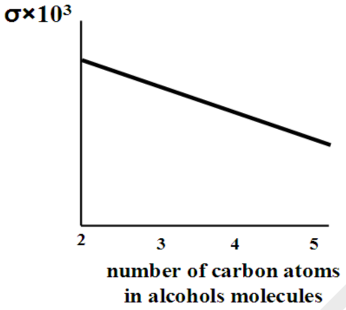


Figure 17.26 — The effect of hydrophobic radicals' length at surface activity of alcohols

Make a conclusion of how the length of hydrophobic radicals affects surface activity of alcohols.

TEST 2. Studying the effect of surfactants concentration at surface tension of solutions

Use stalagmometric method to determine surface tension of amyl alcohol solutions of the following molarity: 0.01, 0.025, 0.05, 0.1, and 0.2 moℓ/ℓ. Write the obtained data into the table 17.5.

Table 17.5 — Surface tension of $C_5H_{11}OH$ with different concentrations

N	Molarity of $C_5H_{11}OH$	Number of drops	$\sigma \times 10^3$, N/m
1	0.01		
2	0.025		
3	0.05		
4	0.1		
5	0.2		

Represent the obtained data in a graph form (figure 17.27).

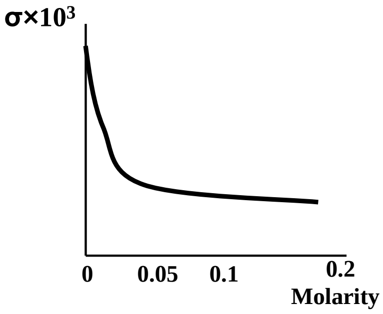


Figure 17.27 — Surface tension isotherm of amyl alcohol

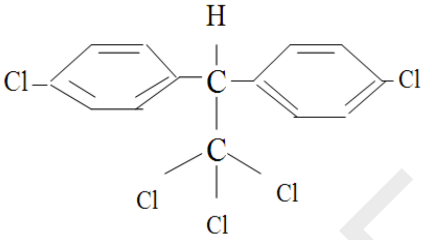
Make a conclusion of how concentration of surfactants affects surface tension of their solutions.

17.10. Problems for the self-control discussion questions

1. Define surface tension. What is the relationship between the intermolecular forces that exist in a liquid and its surface tension?

2. Distinguish between energy state of water molecule at the interface surface and in the interior of the liquid phase.

3. Dichlorodiphenyltrichloroethane (DDT) has the following structure:

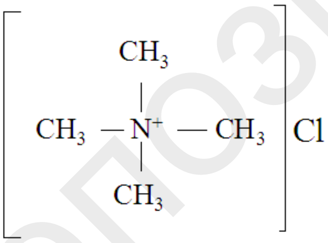


Is this compound hydrophilic or hydrophobic? Is it readily excreted by animals, or will it concentrate in fatty tissues? Does your answer explain why DDT has been banned as a pesticide?

4. Of the following compounds, which will be the best and which will be the worst surfactant? Support your choices with molecular pictures of (a) propionic acid C_2H_5COOH, (b) lauryl alcohol $CH_3(CH_2)_{11}OH$, and (c) sodium lauryl sulfate $CH_3(CH_2)_{11}OSO_3Na$.

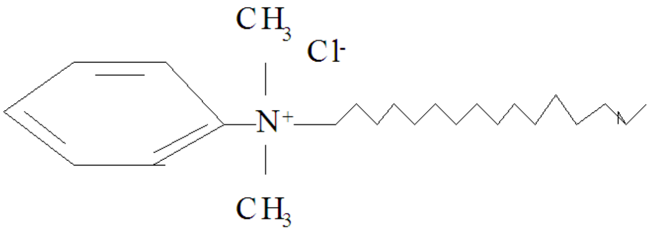
5. Predict which liquid has the greater surface tension, ethanol (C_2H_5OH) or dimethyl ether (CH_3OCH_3)

6. Line drawings of some molecules follow. Identify the hydrophilic and hydrophobic regions of each, and determine which surfactants are.

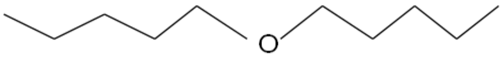


$$\left[\begin{array}{c} CH_3 \\ | \\ CH_3-N^+-CH_3 \\ | \\ CH_3 \end{array}\right]Cl$$

Tetramethylammonium chloride



Benzalkonium chloride used as disinfectant



Dipentyl ether

7. Distinguish between physical and chemical adsorption.

8. Discuss classification of solid adsorbents.

9. Define the main postulates of Langmuir theory of monomolecular adsorption.

10. Define chromatography and classification of chromatographic methods.

NUMERICAL EXERCISES

1. Heat of ammonia adsorption at a dispersed copper is 29.3 kJ/moℓ. What ammonia volume will be absorbed on copper when 158.6 kJ of heat is released? Assume that gas is measured under normal conditions.

Answer: 121.3 ℓ

2. The specific surface area of the activated carbon is 1000 m^2 /g. Calculate a mass of carbon (II) oxide which may be absorbed at 0.10 m^2 of carbon surface when 1 g of carbon adsorbs 0.440 ℓ of CO.

Answer: 55 µg

3. The Molarity of palmitic acid solution is 0.25 mmoℓ/ℓ. The surface tensions of the solution and pure water are 45×10^{-3} and 74.22×10^{-3} N/m, respectively. Calculate the adsorbed amount of palmitic acid at the water/gas interface surface at 10 °C?

Answer: 8.13×10^{-6} moℓ/m^2

4. The relationship between a surface tension of valeric acid solution and its concentration at 80°C is described by the Shishkovsky's equation:

$$\sigma = 62.6 \times 10^{-3} - 17.7\cdot10^{-3} \ln (1 + 19.72\ ^{\circ}C)$$

Calculate the adsorbed amount of valeric acid at the water/gas interface surface when C_M = 0.05 moℓ/ℓ.

Answer: 4.17×10^{-5} moℓ/m^2

5. 0.0001 g of stearic acid form a monolayer at the water/ gas interface, which area is 470 sm^2. Calculate an area occupied by one molecule of stearic acid. Its density is 0.85 g/mℓ and Molar mass is 284 g/mol. Calculate a length of its hydrophobic radical.

Answer: 2.5×10^{-3} µm; 2.2×10^{-19} cm^2

6. The adsorption of a natural dye on the activated carbon is described by the Freundlich's equation: æ = $1.903\times c^{0.7}$. Calculate the mass of a carbon required to extract 90% of a dye from 50 ℓ of a solution. The concentration of a pigment in a solution is 0.04 g/ℓ.

Answer: 9g

7. The adsorbed amount of an adsorbent is 1.8×10^{-3} moℓ/g. How many grams of an adsorbent is it necessary to add to 65 mℓ of a solution in order to decrease its concentration from 0.44 to 0.35 moℓ/ℓ?

Answer: 3.25 g

CHAPTER 18
COLLOIDAL CHEMISTRY

The terms stable and stability
are used in rather special
and often different senses in colloid science:
the relationship between
these usages and the formal thermodynamic
usage is outlined below.

After reading this chapter, you should be able to:

- define dispersed systems and give their classification;
- describe preparing and purification of colloidal solutions (sols);
- discuss the structure of hydrophobic sols micelle;
- discuss coagulation of sols; give reasons for it;
- describe Schulze-Hardy Rule and define critical coagulation concentration.

18.1. Dispersed systems and their classification

Colloidal chemistry is a chemistry of dispersed systems. **A dispersed system is a micro heterogeneous system composed of very fine particles of dispersed phase distributed in a dispersion medium.** A model of a dispersed system is given in figure 18.1.

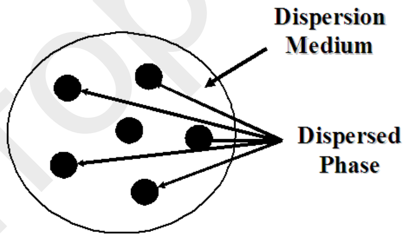


Figure 18.1 — A model of a dispersed system

The dispersed particle is an aggregate consisting of some atoms and molecules. For example, the soap particle contained in a colloidal solution consists of 20–50 molecules each. The colloidal particles are too small to be seen with an ordinary optical microscope. They pass through most filter papers, but can be detected by light-scattering and sedimentation.

Classification of dispersed systems can be done according to the different features.

(1) According to the degree of dispersity they are:

(a) colloidal dispersed $10^{-9} < \alpha < 10^{-7}$m;

(b) coarse dispersed $10^{-7} < \alpha < 10^{-5}$m:

where α is a diameter of a particle of a dispersed phase.

(2) According to the degree of solvation dispersed systems fall into two categories:

(a) lyophilic (for example, dispersions of surfactants and high-molecular compounds);

(b) lyophobic (for example, dispersions of metals and insoluble salts).

In lyophilic colloids dispersed particles are solvated (surrounded by a dense solvate shell which keeps them from clustering). They are stable, their formation is spontaneous. In lyophobic colloids dispersed particles are not solvated therefore they are unstable (their formation is nonspontaneous).

(3) According to interaction between dispersed particles there are two types of dispersed systems:

(a) freely-dispersed colloids are free from interaction between dispersed particles and therefore mobile (aerosols, lyosols);

(b) binding-dispersed colloids involve dispersed particles that are joined together by intermolecular forces and therefore non mobile (foams, jells).

(4) Classification of dispersed systems according to the state of dispersed phase and dispersion medium is given in table 18.1.

Table 18.1 — Classification of dispersed systems according to the state of dispersed phase and dispersion medium

Dispersion medium	Dispersed phase	System	Examples
Gas	Liquid	Liquid in Gas	Fog, clouds, liquid sprays
Aerosols	Solid	Solid in Gas	Smoke, dust
Liquid	Gas	Gas in Liquid	Liquid Foams
Lyosols	Liquid	Liquid in Liquid	Emulsions: milk, mayonnaise
	Solid	Solid in Liquid	Sols, suspensions, colloidal solutions
Solid	Gas	Gas in Solid	Solid foams: bread, activated carbon, expanded polystyrene
Solidosols	Liquid	Liquid in Solid	Opal, pearls
	Solid	Solid in Solid	Pigmented plastics, black diamonds

Considering the data of table 18.1 we come to belief that any object of living and non-living matter may be considered to be a colloidal system (including organs and tissues of a human body). For example, blood carries many substances in colloidal dispersions, including a variety of proteins.

18.2. Preparing and purification of sols

Basically, the formation of dispersed systems involves either degradation of bulk matter or aggregation (condensation) of small molecules or ions. **Dispersion of bulk material** may be done:

- by colloidal mills;
- by ultrasonic;
- by peptization method.

Peptization method is a preparing of sols by addition of electrolytes to a freshly precipitated solid substance that is insoluble in water. Selective adsorption of ions on the surface of solid particles makes them all positively or negatively charged. Repulsion of charged particles results in their migration into a liquid phase. Peptization plays an essential role *in vivo*. For example, dissolution of cholesterol deposits, kidney's and liver's stones proceed under the effect of electrolytes-peptizators applied in medicine as drugs.

Higher degree of dispersion is usually obtained when sol is prepared by aggregation (condensation) methods. **Aggregation** may be physical and chemical.

Physical aggregation involves:

- cooling and pressure elevating of gases and vapors (formation of fogs and clouds in nature);
- substitution of solvents in solutions. For example, a coarse sulfur sol can be prepared by pouring a saturated solution of sulfur in alcohol in water just below boiling point. The alcohol vaporizes, leaving the water insoluble sulfur colloidally dispersed.

Chemical aggregation is based on chemical reactions that occur in aqueous solutions with the formation of solid insoluble substances. In fact all types of chemical reactions can be applied for sols preparing. For example, the colloidal gold dispersion is readily prepared by reducing auric chloride acid by hydrogen peroxide:

$$2\ H[AuCl_4] + 3\ H_2O_2 \rightarrow 2\ Au\downarrow + 8\ HCl + 3\ O_2$$

Radioactive gold dispersion is applied in medicine to treat cancer.

Ion exchange reactions are also applied for sols preparing. For example, colloidal solutions of silver iodide which is a strong antiseptic are prepared by a following reaction:

$$AgNO_3 + KI \rightarrow AgI\downarrow + KNO_3$$

In a human body condensation method prevails over degradation method of sols formation. The only exclusion is emalgation if lipids in intestinal tract.

Colloids always contain electrolytes or other substances from which they ought to be purified. There two main methods of their purification: dialysis and ultrafiltration.

Dialysis has the aim to remove the ionic material that may have accompanied sols formation. It involves special membranes for separating particles of colloidal dimension. Dialysis is a phenomenon like osmosis except that in dialysis not only water molecules but also ordinary-sized ions and molecules can move through the membrane. Colloidally-sized particles are blocked by dialyzing membrane. A simple dialysis set-up is given in figure 18.2.

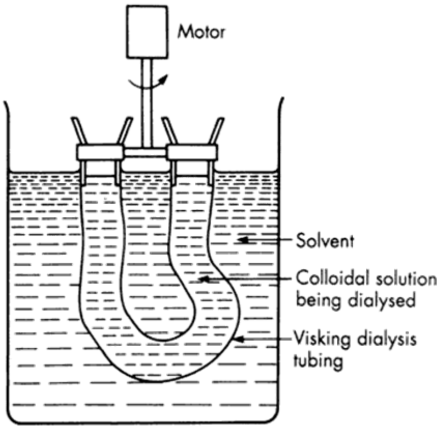


Figure 18.2 — A simple dialysis set-up.

Dialysis is particularly useful for removing small dissolved molecules from colloidal solutions. The only disadvantage of this method is its low rate. A further modification of dialysis is the technique of **electrodialysis.** The applied potential between the metal screens supporting the membranes speeds up the migration of small ions to the membrane surface (figure 18.3).

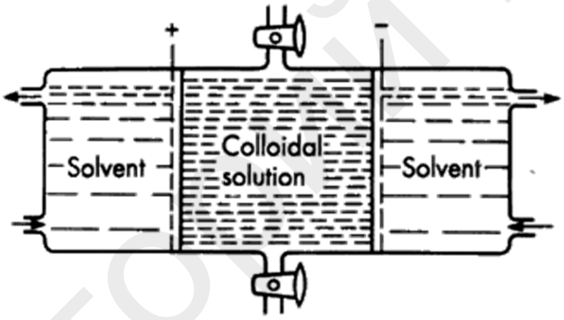


Figure 18.3 — The electrodialysis set-up

Ultrafiltration is the application of pressure or suction to force the solvent and small particles across a membrane while the larger particles are retained. Ultrafiltration is a separation of dispersed phase from a dispersion medium with the help of highly porous membrane (figure 18.4).

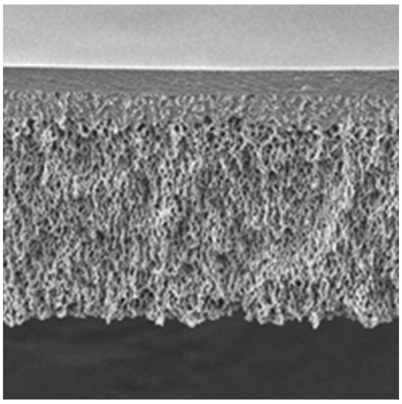


Figure 18.4 — Ultrafiltration disc

This separation process is used in industry and research for purifying and concentrating macromolecular solutions, especially protein solutions. An important application of ultrafiltration is the so-called reverse osmosis method of water desalination. Ultrafiltration is a basic process which proceeds in kidneys. Substances with molar mass less than 10,000 pass across kidney's membrane, while substances with molar mass greater than 50,000 are retained.

Both dialysis and ultrafiltration are involved in **hemodialysis** which is the most common method used to treat advanced and permanent kidney failure (applied in medicine since the 1960s). Hemodialysis means «cleaning the blood» — and that is exactly what this treatment does. Blood is circulated through a machine which contains a **dialyzer** also called an artificial kidney (figure 18.5).

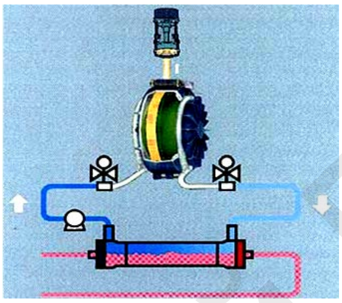


Figure 18.5 — Artificial kidney.

Blood passes on one side of the membrane and dialysis fluid passes on the other. The wastes and excess water pass from the blood through a membrane into the dialysis fluid, which is then discarded. The cleaned blood is returned to a bloodstream.

18.3. Structure of sols

Sols consist of colloidal particles dispersed in water or other solvents. They are not stable because dispersed particles are not solvated. Such systems may exist only in the presence of stabilizers: electrolytes, surfactants and polymers. **Micelle is a solid dispersed particle surrounded by a double electric layer composed of electrolyte-stabilizer ions.** The mechanism of formation of a colloidal solution may be pictured as follows. The molecules of an insoluble product immediately begin to cluster into larger and larger particles. Usually the growth of these particles is very rapid. This process is known as aggregation and it results in an aggregate formation.

An aggregate is a group of particles (which may be atoms or molecules) held together in any way. Under suitable conditions at a definite stage of their growth the particles begin to adsorb the ions contained in the solution. **Potential determining ions (PDI)** are ions which are adsorbed at the surface of aggregates. Their electric charge determines a charge of a colloidal particle. An aggregate and a layer of PDI form a nucleus. **Counter ions** are ions which are adsorbed on the surface of nuclei; they are involved in adsorption and diffusion layers separately.

Colloidal particle is a compartment of a micelle, composed of an aggregate and an adsorption layer. **Adsorption layer** is built up of potential determining ions and counter ions involved into a colloidal particle. **Diffusion layer** involves counter ions that are outside a colloidal particle. At the result of ions adsorption colloidal particles acquire a definite electric charge. The appearance of the charge greatly retards further growth of particles, thus stabilizing sol. Ions adsorption obeys the Panet-Phayans' Rules.

A double electric layer (DEL) is responsible for generation of an electric potential at the boundary between adsorption and diffusion layers. This electrokinetic potential (ξ,) is an important characteristic of sols. ξ – Potential defines stability of a colloidal particle and a distance between cells in vivo.

EXAMPLE 18.1. Let's examine a structure of AgI micelle, when sol is prepared by a reaction:

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

Let's assume that silver nitrate is the excess. An electrolyte in the excess ($AgNO_3$) is responsible for a sol's stability because contributes its ions into formation of a double electric layer around an aggregate:

$$AgNO_3 \rightarrow Ag^+ + NO_3^-$$

An aggregate is built up of m AgI molecules. This salt is a solid substance insoluble in water. According to first Panet-Phayans rule the aggregate may adsorb either silver cations or iodide anions. Since silver cations are the excess they form a PDI layer, giving positive charge for a nucleus. According to second Panet-Phayans rule nucleus attracts nitrate anions as counter ions. The electric charge of a colloidal particle is calculated as a sum of charges of ions involved in its structure:

$$+n -1(n-x) = (+n) – n + x = (+ x).$$

Positively charged colloidal particle attracts the nitrate anions as counter ions of a diffusion layer. The formula of silver iodide micelle stabilized by silver nitrate is given in figure 18.6.

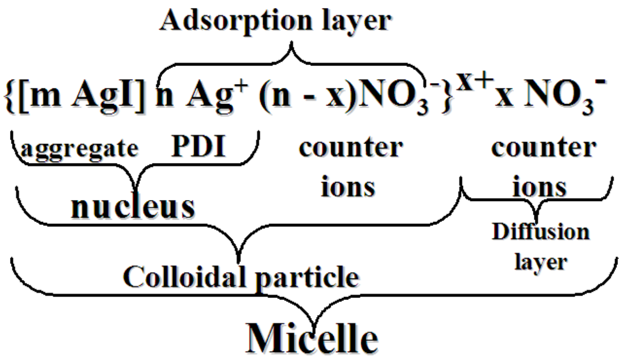


Figure 18.6 — The formula of silver iodide micelle stabilized by silver nitrate

EXAMPLE 18.2 Let’s examine the structure of AgI micelle, when a sol is prepared by a reaction:

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

Let’s assume that potassium iodide is the excess. Thus KI ions stabilize a sol:

$$KI \rightarrow K^+ + I^-$$

These ions form a double electric layer around an aggregate. Electrical charge of a colloidal particle is equal to (- n) + 1(n-x) = (- n) + n – x = (- x).

The formula of silver iodide micelle stabilized by potassium iodide is given in figure 18.7.

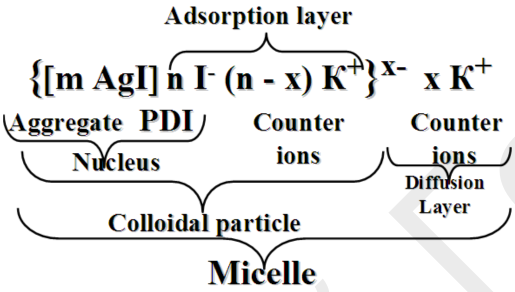


Figure 18.7 — The formula of silver iodide micelle stabilized by potassium iodide

18.4. Physical properties of sols

Three types of physical properties of sols can be distinguished:

- molecular kinetic properties;
- optical properties;
- electro kinetic phenomena.

The most important molecular-kinetics properties are:

(1) Brownian motion — the random chaotic movement of particles in a colloidal dispersion caused by collision between the dispersed particles and the molecules of a dispersion medium (figure 18.8).

Robert Brown (1773–1858), an English botanist, first observed this phenomenon when he saw the trembling of particles inside grains of pollen that he viewed with a microscope.

Figure 18.8 — Brownian motion

(2) Diffusion — a motion of particles down a concentration gradient. Diffusion coefficient (D) depends upon dimension of dispersed particles (r) and viscosity of medium (η):

$$D = \frac{RT}{6\pi\eta r N_A} \tag{18.1}$$

(3) Sedimentation is the settling of suspended particles under the action of gravity. In sols the Brownian motion opposes gravitational settlement which results in a sedimentation equilibrium attainment. Sedimentation equilibrium is responsible for a permanent distribution of dispersed particles. From top to bottom the particles' concentration in sols increases. Sedimentation velocity is an analytical method that measures the rate at which molecules move under the action of gravity. This sedimentation rate provides information about both the mass and the shape of dispersed particles and macromolecules. The rate of erythrocytes' sedimentation is an important diagnostical test.

Dispersed systems exhibit specific **optical properties** due to the equal size of dispersed particles and wavelength of visual spectrum. When a beam of light passes through a colloidal solution each dispersed particle scatters the light rays that fall on it and looks like a luminous point (figure 18.9).

The entire path of a beam becomes visible, having the appearance of a bright cone, if viewed in darkness. This phenomenon is known as the Tyndall effect, after British scientist John Tyndall (1820–1893) (figure 18.10).

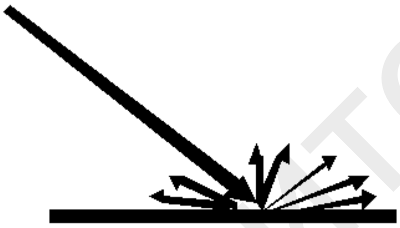


Figure 18.9 — A dispersed particle scatters the light rays that fall on it

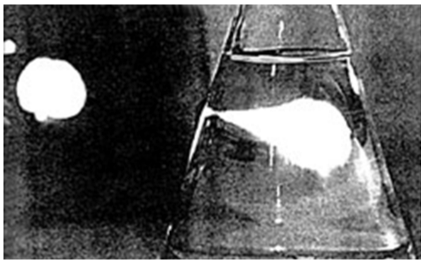


Figure 18.10 — The Tyndall cone

Blue and violet regions of visual spectrum correspond to the shortest wavelength. They are scattered easily by colloidal particles. It defines blue color of a sky. The scattering of light in colloidal solutions is a fundamental property, which depends upon the size, shape, and nature of the colloidal particles, and is therefore expected to reveal the intimate changes taking place in those systems under different conditions. It is possible to investigate the different colloidal-chemical problems by a systematic application of the light-scattering technique. Some of the problems which have been so far investigated are: (1) the mechanism of the formation of colloidal solutions from molecularly dispersed material; (2) phenomena like the ageing and coagulation of sols; (3) studies in soap solutions and gels; (4) mechanism of the swelling of gels, and so on.

Electrokinetic properties of sols appear when electric current is passed through a colloidal solution. The most important among them are electrophoresis and electroosmosis. **Electrophoresis** is the motion of electrically charged dispersed particles under the influence of an electric field. It was first studied and described by F. Reiss in 1807. **Electrophoretic mobility** of a colloidal particle (u) depends upon field strength (E), polarity (ε) and viscosity (η) of a medium (**the Smoluchowski's equation**):

$$u = \xi \frac{\varepsilon E}{k\pi\eta}, \tag{18.2}$$

where k — proportionality coefficient which depends upon a shape of a dispersed particle.

Electrophoresis is wide applied in medicine. For example, **hemoglobin electrophoresis** is a test that measures the different types of hemoglobin in the blood. The test is used primarily to diagnose diseases involving these abnormal forms of hemoglobin, such as sickle cell anemia and thalassemia. **Capillary electrophoresis** (CE) is an analytical technique in which molecules with different electrophoretic mobilities are separated by applying an external electric field. CE has applications to drug discovery and screening, clinical analysis, and pathogen detection. **A microanalytical electrophoresis technique** is used for the determination of polymorphic blood proteins for medical and forensic applications.

Electroosmosis is an electrical transfer of dispersion medium across semipermeable membrane. Its application in medicine is limited. It is applied in medicine for therapeutic sera purification.

18.5. Coagulation of sols

The terms stable and stability are used in rather special and often different senses in colloidal science. Thermodynamically stable means that the system is in a state of equilibrium corresponding to a local minimum of the Gibbs energy. **Colloidally stable** means that the particles do not aggregate at a significant rate. The main stability factors for sols are kinetic and aggregative.

Brownian motion is responsible for kinetic stability of sols and electric charge of dispersed particles is responsible for sols aggregative stability. The destruction of aggregative stability of sols results in their coagulation.

Coagulation is the irreversible aggregation of dispersed particles into large particles followed by rapid precipitation. It is a spontaneous process which results in a decrease in Free Gibbs Energy of a system. Sol coagulates when heated or under the mechanical disturbance but the chief reason for their coagulation is addition of electrolytes. Coagulation by electrolytes plays an essential role in vivo because colloidal solutions of cells are in contact with electrolytes, contained in biological fluids.

The introduction of an electrolyte into the solution increases the total concentration of ions in it, creating favorable conditions for the charged colloidal particles to absorb ions of the opposite sign. The initial charge of particles decreases or is neutralized altogether, after which coagulation of sols sets in.

Critical coagulation concentration (γ) is a minimal amount of an electrolyte which starts coagulation in 1 L of a sol. It is calculated by the following equation:

$$\gamma = \frac{C \times \mathrm{V}}{\mathrm{V_S}}, \tag{18.3}$$

where c — concentration of an electrolyte, mol/ℓ;

V — a volume of an electrolyte solution, mℓ;

V_S — a volume of a sol, ℓ.

Schulze-Hardy Rule postulates **that hydrophobic colloids are coagulated most efficiently by ions of opposite charge and high charge number**. The Nobel Prize winners B. Derjaguin and L. Landau proved that critical coagulation concentrations of ions that initiate coagulation of lyophobic sols relate to each other as their reverse charges raised into the power six:

$$\gamma_1 : \gamma_2 : \gamma_3 = \frac{1}{1^6} : \frac{1}{2^6} : \frac{1}{3^6} = 730 : 11 : 1 \tag{18.4}$$

Schulze-Hardy Rule fails to give the exact description of coagulation since it doesn't take in view the effect of ionic radii on coagulating activity of ions**.** Ions of the same charge but different ionic radii are arranged in lyotropic series:

$$\underrightarrow{\mathbf{Li^+} \quad \mathbf{Na^+} \quad \mathbf{K^+} \quad \mathbf{Rb^+} \quad \mathbf{Cs^+}}$$

Increase in radius gives increase in coagulating activity of ions

Coagulation is characterized by its rate. The rate of coagulation is defined as the change in a number of dispersed particles in one liter of a colloidal solution per time unit. The rate of coagulation depends upon both electrolyte and sol concentration. The kinetic curve of sols coagulation is given in figure 18.11.

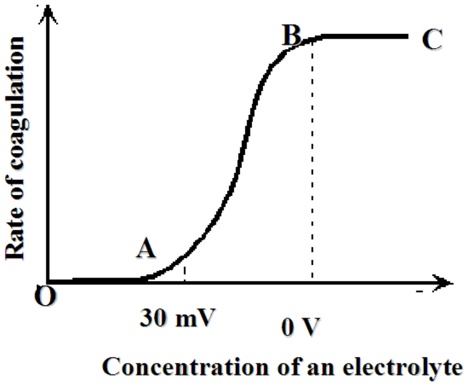


Figure 18.11 — The kinetic curve of sols coagulation

A segment OA corresponds to the period of a slow coagulation, when sol is rather stable. A segment AB corresponds to the period of a visible coagulation, which starts when ξ-potential of a sol becomes only 30 mV. A segment BC corresponds to the period of a rapid coagulation (ζ-potential of a sol is zero).

When sol is coagulated by a mixture of electrolytes the following phenomena may occur:

(a) **additivism** — the phenomenon where two ions in combination summarize their coagulating activity;

(b) **antagonism** — the phenomenon where two ions in combination have a coagulating effect which is less than that predicted from their individual effects;

(c) **synergism** (from the Greek «*synergos*», meaning working together) refers to the phenomenon in which two or more ions acting together create an effect greater than that predicted by knowing only the separate effects of the individual ions.

Before injecting an electrolytes' mixture a doctor must know that they are not synergists in order to avoid a harmful coagulation of blood. Before electrolytes application as a drug a doctor must take into consideration not only their concentration but the electric charge of their ions. For example, physiological NaCl solution can't be changed by $MgCl_2$ solution, because Mg^{2+} exhibits high coagulating activity.

Coagulation can also be brought about by the other colloids with opposite charges of their particles. The coagulation of colloids by one another has found a very important use in purification of drinking water.

18.6. Laboratory work colloidal solutions

TEST 1. Preparing of $Fe(OH)_3$ sol by $FeCl_3$ hydrolysis.

Pour 150 mℓ of distilled water into a flask and heat it up to the boiling point using an electric heater. Add 5 mℓ of concentrated $FeCl_3$ solution into boiling water. Use an analytical pipette to measure this volume. At the result a dark-brown $Fe(OH)_3$ sol is prepared. Cool the prepared sol by tap water.

Write the equation for $FeCl_3$ hydrolysis. Write the formula for micelle of a prepared sol. Give name to all the compartments of a micelle.

TEST 2. Coagulation of $Fe(OH)_3$ sol.

In order to determine a critical coagulation concentrations (γ) of $Fe(OH)_3$ sol it is necessary to prepare electrolyte solutions with increasing concentrations of salts. For this purpose take three sets of test tubes each containing six test tubes. Fill each test tube with water and electrolyte solution according to the table 18.2. After that add 5 mℓ of $Fe(OH)_3$ sol to each test tube. Time of exposition is 20 minutes. After that time examine solutions in the test tubes and mark presence or absence of coagulation in them by signs «+»or «–».

Critical coagulation concentration is calculated according to the equation:

$$\gamma = C \times V \times 100 \qquad (18.5)$$

where C — concentration of electrolytes, mol/ℓ;

V — the minimum volume of electrolyte that initiates coagulation of a sol, mℓ.

Table 18.2 — $Fe(OH)_3$ coagulation under the influence of electrolytes

A set of test tubes	**Coagulator**		**Critical coagulation concentration mmol/ℓ**	Number of a test tube					
	Electrolyte	Ion		1	2	3	4	5	6
1	3.0 M KCl	Cl^-							
2	0.005 M K_2SO_4	SO_4^{2-}							
3	0.0005 M $K_3[Fe(CN)_6]$	$[Fe(CN)_6]^{3-}$							
Volume, ml	Distilled water			0	1	2	3	4	4,5
	Electrolyte solution			5	4	3	2	1	0,5
	$Fe(OH)_3$ sol			5	5	5	5	5	5

Use the data of table 18.2 to calculate the critical coagulation concentrations of KCl, K_2SO_4 and $K_3[Fe(CN)_6]$ solutions. Compare the results of yours calculations with Schulze-Hardy Rule. Explain the discrepancy in experimental and theoretical data.

18.7. Problems for the self-control

DISCUSSION QUESTIONS

Distinguish between colloidal dispersed and coarse dispersed solutions.

What simple test could be used to tell if a clear, colorless solution contained substances in colloidal dispersion?

Distinguish between lyophilic and lyophobic colloidal systems. Give the examples.

Identify the following terms: (a) dialysis, (b) electrodialysis, (c) ultrafiltration.

Distinguish between degradation and condensation methods of sols preparing.

The blood is simultaneously a solution, a colloidal dispersion, and a suspension. Explain.

What causes the Brownian motion?

What is an emulsion? Give some examples.

What is a sol? Give some examples.

NUMERICAL EXERCISES

11. Barium sulfate sol was prepared by mixing aqueous solutions of barium nitrate and potassium sulfate according to the equation:

$$Ba(NO_3)_2 + K_2SO_4 \rightarrow BaSO_4 + 2\ KNO_3$$

Write the formulas for micelles of sols, prepared:

a. When barium nitrate was the excess.

b. When potassium sulfate was the excess.

Name all the compartments of micelles.

12. Magnesium (II) hydroxide sol was prepared by interaction of magnesium (II) chloride dilute solution and slight excess of sodium hydroxide according to the equation:

$$MgCl_2 + 2\ NaOH \rightarrow Mg(OH)_2 + 2\ NaCl$$

Write the formula for a micelle of a prepared sol and answer the following questions:

a. What is the charge of a colloidal particle?

b. Towards what electrode this particle is drawn when a current is passed through the solution?

c. What electrolyte $AlCl_3$ or Na_3PO_4 exhibits the smallest critical coagulation concentration for this sol?

13. Calcium carbonate sol was prepared by mixing aqueous solutions of calcium chloride and potassium carbonate according to the equation:

$$CaCl_2 + K_2CO_3 \rightarrow CaCO_3 + 2\ KCl$$

Write the formulas for micelles of sols, prepared when:

a. Calcium chloride was the excess.

b. Potassium carbonate was the excess.

Name all the compartments of micelles.

14. Iron (III) hydroxide sol was prepared by interaction of Iron (III) nitrate dilute solution and slight excess of potassium hydroxide according to the equation:

$$Fe\ (NO_3)_3 + 3\ KOH \rightarrow Fe\ (OH)_3 + 3\ KNO_3$$

Write the formula for a micelle and answer the following questions:

a. What is the charge of a colloidal particle?

b. Towards what electrode (anode or cathode) this particle is drawn when a current is passed through the solution?

c. What electrolyte $FeCl_3$ or Li_3PO_4 exhibits the smallest critical coagulation concentration for this sol?

15. Prepare lead (II) chloride sol according to the reaction:

$$Pb(NO_3)_2 + 2\ KCl \rightarrow PbCl_2 + 2\ KNO_3$$

Write the formula of a prepared micelle when $Pb(NO_3)_2$ is the excess. Give name to all the compartments of a micelle.

16. Prepare As_2S_3 sol according to the reaction:

$$2\ H_3AsO_3 + 3\ H_2S \rightarrow As_2S_3 + 6\ H_2O$$

Write the formula of an obtained micelle when H_2S is the excess. Give name to all the compartments of a micelle.

17. Prepare $Al(OH)_3$ sol according to the reaction:

$$3\ Ba(OH)_2 + 2\ AlCl_3 \rightarrow 2\ Al(OH)_3 + 3\ BaCl_2$$

Write the formula of a prepared micelle when $AlCl_3$ is the excess. Towards what electrode (anode or cathode) this particle is drawn when a current is passed though the solution?

18. Prepare $CaCO_3$ sol according to the reaction:

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl$$

Write the formulas for micelles of sols, prepared

a. When $CaCl_2$ is the excess.

b. When Na_2CO_3 is the excess.

19. What ions will coagulate a prepared sol: K^+, Ca^{2+}, Cl^-, Al^{3+}, $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$? Arrange the ions in a serious of increasing ability to initiate a coagulation process.

20. Fine radioactive particles are contained in drinking water. It was decided to purify water by addition of electrolytes. What electrolyte: $AlCl_3$ or Na_3PO_4 is preferable? It was determined that in electric field the particles migrate towards cathode.

CHAPTER 19
MACROMOLECULES AND THEIR SOLUTIONS

If you want to understand function,
study structure.

Francis H. Crick

After reading this chapter, you should be able to:

- define macromolecules and their classification;
- describe swelling and dissolution of polymers in different solvents and under different conditions;
- describe structure and specific properties of polyelectrolytes at isoelectric point;
- discuss methods of pI focusing;
- define protected colloids.

There are macromolecules everywhere, inside and outside us. Life in all its forms, from its intrinsic nature to its technological interaction with its environment, is the chemistry of macromolecules. **A macromolecule** is a chemical species distinguished by a high molar mass (10^4–10^{10} g/mol). Their molecules length is approximately 10^{-6} m. The chemistry of macromolecules, which are called **polymers**, differs greatly from the chemistry of small, ordinary molecules. Studying the properties of these giant molecules requires special techniques.

19.1. Macromolecules and their classification

Polymers may be classified according to their origin. Some of them are **natural.** They include polysaccharides such as cellulose, polypeptides such as protein enzymes, and polynucleotidic such as deoxyribonucleic acid (DNA). Others are **synthetic;** they are manufactured by stringing together and (in some case) cross-linking smaller units known as monomers. Synthetic polymers may be prepared by polymerization or polycondensation reactions. For example, teflon production is an example of polymerization reaction:

$$n\ F_2C{=}CF_2 \rightarrow [-F_2C - CF_2 -]_n.$$

Teflon is applied to prepare cooking utensils, electrical insulation, and also blood vessels and heart’s vents for transplantation (figure 19.1).

Figure 19.1 — Heart’s vents for transplantation

Polyethylene production is also an example of polymerization reaction:

$$n\ CH_2{=}CH_2 \rightarrow [–CH_2–CH_2–]_n$$

Polyethylene is applied in medicine to prepare films, tubes and bottles.

Nylon which is a product of adipic acid and hexamethylenediamine polycondensation is used as sewing material in surgery. Its synthesis can be represented by a scheme:

$$n\ HOOC\text{-}(CH_2)_4\text{-}COOH + n\ H_2N\text{-}(CH_2)_6\text{-}NH_2 \rightarrow$$
$$\rightarrow [\text{-}CO\text{-}(CH_2)_4–CO\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}]_n + n\ H_2O.$$

Another way to classify polymers is according to the values of their molar masses. Monodispersed and polydispersed high molecular compounds are distinguished.

Monodispersed compounds are polymeric systems whose molecules have equal molar masses (for example, hemoglobin and some other proteins). **Polydispersed** compounds are polymeric systems whose molecules have different molar masses (for example, DNA and rubbers). The molar mass for such polymers may be defined in different ways. The two most common definitions are:

(a) Number-Average Molar Mass:

$$M_r(\text{number average}) = \frac{\Sigma n_i M_{r,i}}{\Sigma n_i} \tag{19.1}$$

where n_i is the number of molecules of relative molecular mass $M_{r,I}$;

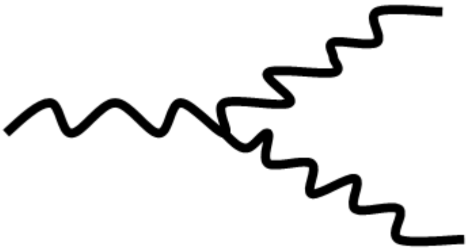
(b) Weighted-Average Molar Mass:

$$M_r(\text{mass average}) = \frac{\Sigma n_i M_{r,i}^2}{\Sigma n_i M_{r,i}} \tag{19.2}$$

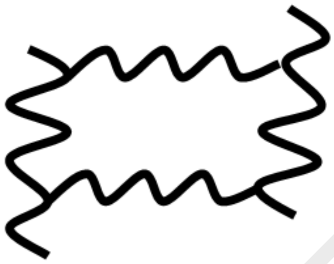
For any polydispersed system weighed average molar mass is greater than number-average molar mass, and only when the system is monodispersed will these averages coincide. The ratio **mass average/number average** is a measure of the degree of polydispersity.

According to the configuration of macromolecules four types of polymers may be distinguished. The first category of polymers has **long threadlike straight molecules**. Such compounds are named linear polymers**.** For example, gelatin and natural rubbers:

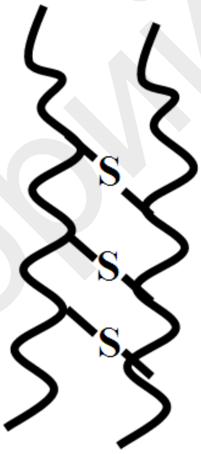
The second category of polymers exhibits **branched-chain configuration** of their molecules (for example, starch and glycogen):



The third category of polymers has **three-dimension molecules** (for example, phenol formaldehyde resins):



The fourth category of polymers exhibits sewn cross-linked configuration of macromolecules (for example, vulcanized rubber).



The specific properties of polymers are:

- **flexibility** (due to rotation about carbon-carbon and other bonds;
- **strong intermolecular forces.**

19.2. Polymers solutions

Polymers may form true and colloidal solutions. True solutions are formed when a polar polymer is dissolved in a polar solvent (protein in water) or when a non-polar polymer is dissolved in a non-polar solvent (rubber in benzene).

The first step in polymers dissolving process is swelling. **Swelling is a spontaneous irreversible diffusion of solvent molecules into a polymer phase.** Molecules of a polymer do not diffuse into a solvent because of their low mobility caused by high molar mass and strong intermolecular forces (figure 19.2).

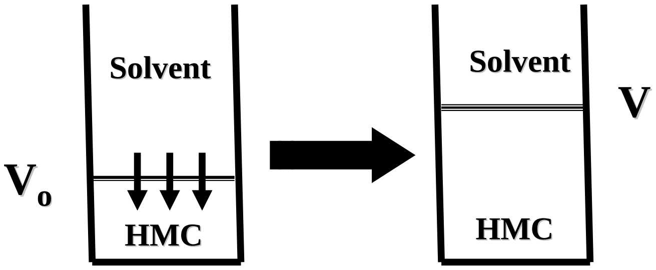


Figure 19.2 — The first step in polymers dissolving process is swelling

Swelling results in increase of volume and mass of a polymer. **Swelling percent** (α) may be calculated as:

$$\alpha = \frac{V - V_o}{V_o} \times 100 \qquad (19.3)$$

where V_o is an initial volume of a polymer, mℓ;
V is a volume of a polymer after swelling.
Another way to calculate swelling percent is:

$$\alpha = \frac{m - m_o}{m_o} \times 100 \qquad (19.4)$$

where m_o is an initial mass of a polymer, g;
m is a mass of a polymer after swelling.

Two types of swelling are distinguished: (a) limited and (b) non-limited. The kinetic curves of swelling are represented in figure 19.3.

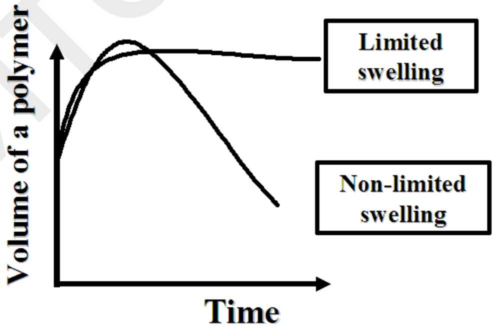


Figure 19.3 — Kinetic curves of swelling

Limited swelling results in gels formation (for example, gelatin in cold water). Gel is a state of matter intermediate between solids and liquids. **Non-limited swelling** results in formation of true solutions, which are stable systems (for example, gelatin in hot water).

Swelling is an important physiological process. Skin, brain and eye tissues are able to swell. Swelling percent may change as the result of inflammation or trauma (figure 19.4). Aging decreases a swelling percent of tissues.

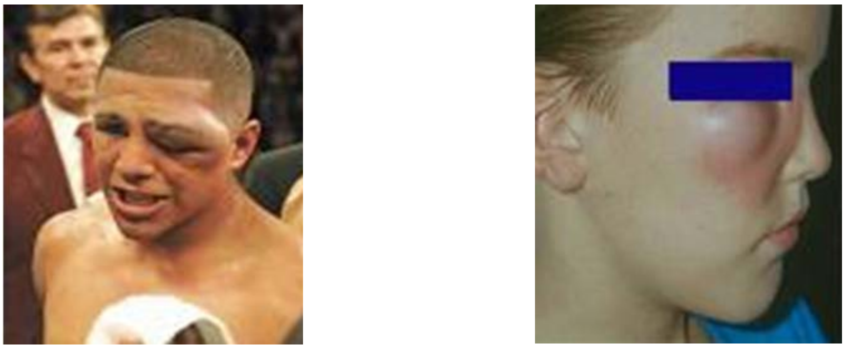


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Figure 19.4 — Swelling percent may change as the result of inflammation or trauma.

Swelling is affected by different factors:

(a) **nature** of a macromolecules and nature of a solvents: «Like dissolves like»;

(b) **configuration** of chains. Linear and branched polymers exhibit higher swelling percent than three-dimension and cross-linked compounds;

(c) **acidity** of a medium (for amphiprotic polyelectrolytes only);

(d) **temperature.** The higher is temperature, the greater is swelling percent of a high-molecular compound. Increase in temperature gives increase in a rate of solvents diffusion into a polymer;

(e) **presence of electrolytes**. They may affect polymers solubility in two different ways: (1) *salting-in effect* — the increase in solubility under the influence of electrolytes; (2) *salting-out effect* — the decrease in solubility under the influence of electrolytes.

19.3. Polyelectrolytes

Polyelectrolytes are polymers which contain ionizable groups. They fall into three categories: acid, base and amphiprotic. **Acid polyelectrolytes** contain ionosable groups that are proton donors (for example, carboxylic and sulphonic groups):

$$-\,COOH \rightleftharpoons -\,COO^- + H^+$$
$$-\,SO_3H \rightleftharpoons -\,SO_3^- + H^+$$

Base polyelectrolytes contain ionizable groups that are proton acceptors (for example, an amino group):

$$-\,NH_2 + H^+ \rightleftharpoons -\,NH_3^+$$

Amphiprotic polyelectrolytes contain both acid and base ionizable groups. The bright example of such polyelectrolytes is proteins. Protein's simplified formula may be represented as **$NH_2 - R - COOH$**.

An important feature of proteins and some other biopolymers is that their overall charge depends on the pH of medium. Under physiological conditions (pH = 7.4) proteins exist as dipolar ions **$NH_3^+ -R-COO^-$,** the net electric charge of their molecules is zero. In acidic environments protons attach to basic groups and the net charge is positive (cationic form). In basic media the net charge is negative as the result of proton loss (proteins turn into anionic forms.) The acid-base equilibrium in proteins solutions is represented in figure 19.5.

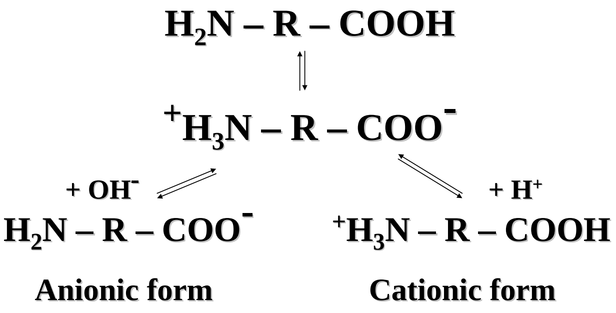


Figure 19.5 — The acid-base equilibrium in proteins solutions

Proteins exhibit their specific properties at the isoelectric state, which is characterized by the zero net electric charge of macromolecules:

$$NH_3^+ – R –COO^-$$

Isoelectric point (pI) is the pH of a solution at which the net charge on a macromolecule is zero. Isoelectric point is an important characteristic of each protein. Some of them are given in the table 19.1.

Table 19.1 — Isoelectric point of same proteins

Protein	**pI**
Hemoglobin	6.7
Bovine serum albumin	4.9
Carboxypeptidase	6.0
Cytochrome c	10.7

Above 85% of proteins have pI in the range of 4.5 to 8.5 (figure 19.6).

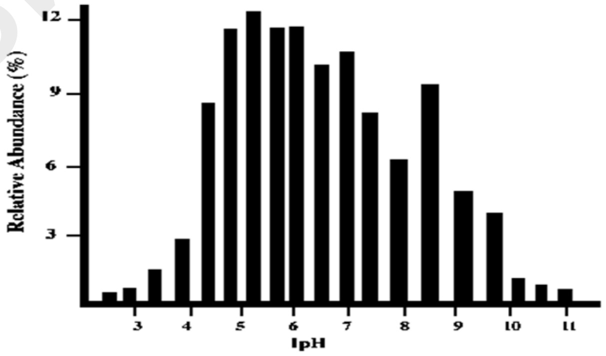


Figure 19.6 — Isoelectric points of most proteins

At isoelectric state a protein molecule coils about itself in a spiral manner to form a helix (α-helix configuration). When pH of a solution is greater than pI or lower than pI a protein molecule becomes linear due to repulsion of charged functional groups (NH_3^+ in acid solutions and COO^- in base solutions). A unique configuration of a protein molecule at isoelectric state is responsible for its specific physical and chemical properties (figure 19.7).

The specific physical properties of proteins at isoelectric state are:

- minimum swelling percent;
- maximum coagulation percent;
- zero electrophoretic mobility.

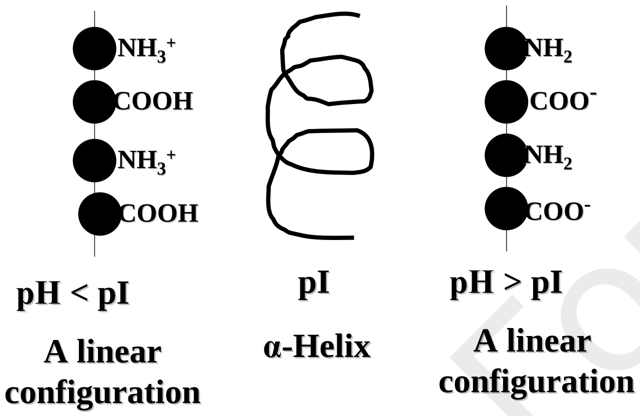


Figure 19.7 — Configuration of protein molecule in solutions with the difference pH values

Let us review the **experimental methods of pI focusing**. First of all we can determine isoelectric points of proteins by measuring their swelling percents in solutions with the different pH values. pI corresponds to the minimum swelling percent (figure 19.8).

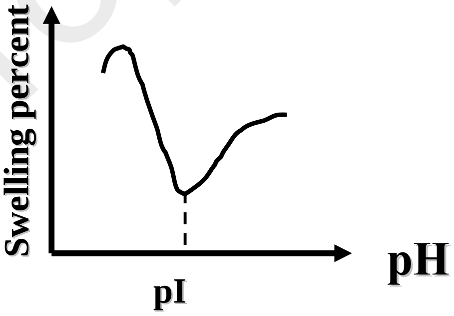


Figure 19.8 — Swelling percents of proteins in solutions with the different pH values

Another way to focus pI is measuring of proteins coagulation percent in solutions with the different pH values. Coagulation (denaturation) of polymers solutions may be caused by addition of electrolytes or addition of non-solvents. Non-solvents are liquids in which a particular polymer exhibits very low solubility. Both factors cause desolvation of macromolecules by binding solvent's molecules thus decreasing a density of a solvate shell around polymers. Maximum coagulation percent corresponds to isoelectric state of a protein (figure 19.9).

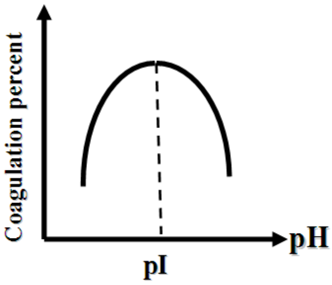


Figure 19.9 — Coagulation percents of proteins in solutions with the different pH values

One of the most accurate methods of pI focusing is the measuring of proteins electrophoresis mobility in solutions with different pH values. **Electrophoresis** is the migration of charged molecules in a solution in response to an electric field. At isoelectric state electrophoresis mobility equals to zero (u = 0) because the net electric charge of a macromolecule is zero. Positive signs of electrophoresis mobility indicate travel of charged macromolecules towards cathode, and negative signs of electrophoresis mobility indicate travel of charged macromolecules towards anode. The curve of proteins electrophoresis mobility is given in figure 19.10.

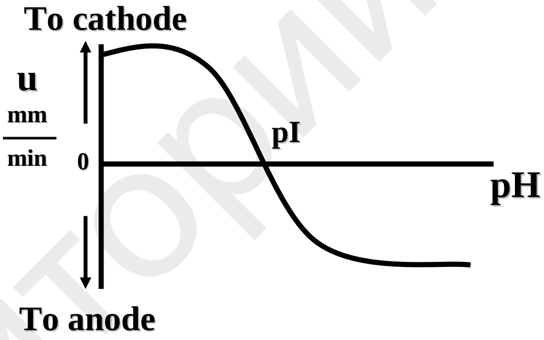


Figure 19.10 — The curve of proteins electrophoresis mobility

Electrophoresis is used not only to focus pI of proteins but to separate their mixtures into fractions.

19.4. Protected colloids

Addition of high concentrations of hydrophilic colloids (surfactants and macromolecules) usually protects the hydrophobic sols from coagulation. This phenomenon is called **protective action.** Colloidally stable mixtures of a lyophobic and lyophilic colloid are called **protected lyophobic colloids**. Macromolecules and surfactants adsorb on the surface of dispersed particles turning lyophobic systems into lyophilic, which are stable due to solvation.

The ability of surfactants and macromolecules to protect sols is characterized by gold, silver and some other numbers. **«Gold number» is a minimal mass of**

a surfactant or polymer which is required to protect 10 mℓ of gold dispersion from coagulation by 1 mℓ of 10 % NaCl solution. «Gold number» of cerebrospinal fluid is used as a test on meningitis (table 19.2).

Protective action of lyophilic colloids is responsible for stability of dispersed systems in blood and other biological fluids. For example, proteins of blood stabilize dispersions of lipids, cholesterol and insoluble salts preventing their sedimentation.

Table 19.2 — «Gold numbers» of some polymers

Polymers	**«Gold number», mg**
Gelatin	0.008
Hemoglobin	0.05
Casein	0.01
Starch	25

When a protective action of proteins is decreased it results in atherosclerosis, calcinosis, podagra, formation of stones in kidneys and liver.

Atherosclerosis is a killer number one in the world, especially in high developed countries. When cholesterol content is high in bloodstream, the excess is deposited in arteries, making them narrow. As the result the coronary arteries become narrowed by cholesterol deposits and cannot supply enough blood to the heart. The result is coronary heart diseases. Three stages in atherosclerosis can be distinguished (figure 19.11):

Figure 19.11 — Three stages in atherosclerosis

The protective action of proteins is responsible for high content of gases (O_2 and CO_2) in blood. The protective action of proteins is applied in pharmacological industry to stabilize medical dispersions of silver, gold, mercury and their radioactive isotopes.

19.5. Laboratory work polymers' solutions

TEST 1. Determining of rubber swelling percent in various solvents

Weigh the four rings of rubber and put them in sample bottles filled with various solvents (a) water, (b) benzene, (c) turpentine oil, (d) hexane. After 30 minutes take the rings out of the solutions and weigh them again. Write the initial and final masses of rubber into the table 19.3. Calculate swelling percents of a rubber using the formula:

$$\alpha = \frac{m - m_o}{m_o} \times 100$$

where m_o — initial mass of a rubber, g;
m — mass of a rubber after swelling.

Table 19.3 — The effect of solvents polarity at swelling percent of rubber

Solvents	**Initial mass of a rubber, m_o, g**	**Mass of a rubber after swelling, M, g**	**$m - m_o$**	**Swelling percent of a rubber, α**
Water				
Turpentine oil				
Benzene				
Hexane				

Draw conclusions about how the polarity of the solvent affects the degree of rubber swelling.

TEST 2. Effect of medium acidity on the swelling percent of gelatin

Add 0.5 mℓ of gelatin into the four test tubes and pour 10 mℓ of solvents according to the scheme:

the first test tube	0.1M HCl	pH = 1
the second test tube	a buffer solution	pH = 4.7
the third test tube	distilled water	pH = 7
the fourth test tube	0.1 M NaOH	pH = 13

Mix the solutions with a glass rod. After 30 minutes measure the gelatin volume and calculate its swelling percent according to the formula:

$$\alpha = \frac{V - V_o}{V_o} \times 100$$

where V_o — initial volume of a gelatin, mℓ;
V — volume of a gelatin after swelling.
Write the initial and final volumes of gelatin into the table 19.4.

Table 19.4 — The effect of medium acidity at swelling percent of gelatin

Solvent	**pH**	**V_0, mℓ**	**V, mℓ**	**$V - V_o$**	**Swelling percent of a gelatin, α, %**
0.1M HCl	1	1.0			
A buffer solution	4.7	1.0			
Distilled water	7	1.0			
0.1 M NaOH	13	1.0			

Represent the obtained data in graph form (plot of swelling percent α versus pH of solutions). Determine isoelectric point of gelatin. Make a conclusion.

TEST 3. Isoelectric point of a protein focusing

Take 5 centrifuge test tubes and fill them with 1 mℓ of acetate buffer solution ($CH_3COOH + CH_3COONa$) according to the scheme:

the first test tube pH = 3.8,
the second test tube pH = 4.1,
the third test tube pH = 4.7,
the fourth test tube pH = 5.3
the fifth test tube pH = 6.2.

Add 0.5 mℓ of 1 % bovine serum albumin (BSA) solution and 1 mℓ of acetone (use analytical pipettes) into each test tube. Stir the prepared solutions and determine turbidity in each test tube giving marks from 0 up to 5. Write the obtained data into the table 19.5. The highest turbidity corresponds to the maximum protein's coagulation and its isoelectric point.

In order to get more accurate results separate the protein's precipitate and solutions using a centrifuge. Pour a liquid above the precipitate into other test tubes and add 2 mℓ of the biuret reagent ($CuSO_4 + NaOH$) into each of them. After the precipitate is dissolved in the reagent compare intensity of the violet color in each test tube using marks from 0 up to 5. Write the obtained data into the table 19.5.

Table 19.5 — Isoelectric point of a protein focusing

pH	**3.8**	**4.1**	**4.7**	**5.3**	**6.2**
Degree of turbidity					
Intensity of a color					

A sample with the highest turbidity and lowest intensity of color corresponds to isoelectric point of a protein.

19.6. Problems for the self-control

DISCUSSION QUESTIONS

1. Define high molecular compounds or polymers. Give the examples of natural and synthetic polymers.

2. Distinguish between Number-Average Molar Mass and Weighted-Average Molar Mass of polymers.

3. Classify macromolecules according to configuration of their chains.

4. What factors affect swelling and dissolving of high molecular compounds?

5. Distinguish between acid, base and amphiprotic polyelectrolytes.

6. Define isoelectric point of proteins. What are the experimental methods of its focusing?

7. Define protected colloids. Explain the biological role of proteins protective action in blood.

NUMERICAL EXERCISES

1. A polydispersed solution has the following distribution:

Number of Molecules	Molar Mass, g/mol
10	25,000
7	17,000
24	31,000
16	49,000

Calculate the values of both Number-Average Molar Mass and Weighted-Average Molar Mass.

2. The initial mass of a rubber was 10 g. After swelling in benzene its mass became equal 22 g, and after swelling in toluene — 41.4 g. In what solution the swelling percent of a rubber was higher?

3. In what solvent — water, alcohol, benzene or physiological solution — gelatin exhibits the highest swelling percent? Explain your answer.

4. pI of gelatin is 4.7. Gelatin was dissolved in a solution with protons (H$^+$) concentration 1000 times higher than that in pure water. What electric charge (positive or negative) will gain gelatin's molecules in this solution?

5. In what pH range is it better to separate proteins by electrophoresis if their isoelectric points are 4.8 and 7.9 respectively. Explain your answer.

6. pI of albumin is 4.8. Albumin was dissolved in a buffer solution with [H$^+$] = 10^{-6} mol/ℓ. Toward what electrode protein molecules will migrate in the electric field?

7. At pH equal to 6, insulin migrates neither to cathode, nor to anode in the electric field. Toward what electrode it will move in the electric field when dissolved in 0.1 mol/ℓ hydrochloric acid solution?

8. A mixture contains an enzyme A (pI = 5) and an enzyme B (pI = 9). In what pH range it is possible to separate the enzymes by electrophoresis?

9. The electrophoretic mobility (u) of bovine serum albumin (BSA) under the influence of an electric field in aqueous solution was monitored at several values of pH, and the data are listed below (opposite signs indicate opposite directions of travel). What is the isoelectric point of the protein?

pH	4.20	4.56	5.20	5.65	6.30	7.00
u (μm s^{-1})	+0.50	+0.18	–0.25	–0.65	–0.90	–1.25

Multiple Choice Questions

13. ELECTRONIC STRUCTURE OF ATOMS

1. What is the difference between the atoms that are isotopes of one element?
(a) they differ by the number of neutrons;
(b) they differ by the number of electrons;
(c) they differ by the number of protons;
(d) they differ by the electric charge of nuclei.

2. Point out the number of neutrons in the nucleus of $^{235}_{92}U$:

(a) 235 (b) 92 (c) 143 (d) 327

3. Point out a number of protons in the molecule of nitrogen (II) oxide:
(a) 30 (b) 15 (c) 14 (d) 16

4. The principal quantum number describes:
(a) an atomic orbital;
(b) a number of electrons in an atom;
(c) the orientation of an orbital in space;
(d) the total energy of an electron.

5. The magnetic quantum number describes:
(a) the total energy of an orbital;
(b) a number of orbitals within a subshell;
(c) the orientation of the orbital in space;
(d) two possible spinning motions of an electron.

6. The distribution of electrons in atomic orbitals is determined by:
(a) the Pauli's exclusion principal;
(b) the Hund's rule;
(c) the principal of minimum energy;
(d) all of the principles given above.

7. The Pauli's Exclusion Principle postulates that
(a) no two electrons in an atom can have the same four quantum numbers;
(b) the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins;
(c) the atomic orbitals that have the same energy are said to be degenerate;
(d) the exact momentum and position of the electron cannot be simultaneously determined.

8. Electron Affinity is:

(a) the ability of an atom to attract electrons toward itself in a chemical bond;

(b) a theoretically calculated distance from the nucleus to the maximum of electron density in the outer orbital;

(c) the minimum amount of energy required to remove an electron from an atom;

(d) the energy change that occurs when an electron is accepted by an atom to form an anion.

9. Electronegativity of an atom is defined as:

(a) the ability of an atom to attract electrons toward itself in a chemical bond;

(b) the maximum amount of energy required to remove an electron from an atom;

(c) the minimum amount of energy required to add an electron to an atom;

(d) the energy change that occurs when an electron is removed from an atom to form a cation.

10. Indicate a serious where the orbitals are listed in order of increasing energy:

(a) 2s, 2p, 2d; (b) 3s, 3p, 3d;

(c) 4f, 5s, 6d; (d) 3p, 3d, 3f.

11. How many of electrons in atom with electron configuration …$3d^5$ $4s^2$?

(a) 20(b) 23(c) 25(d) 30

12. The electron configuration for Vanadium atom is

(a) $1s^22s^22p^63s^23p^64s^24p^3$ (b) $1s^22s^22p^63s^23p^63d^34s^2$

(c) $1s^22s^22p^63s^23p^64s^23d^5$ (d) $1s^22s^22p^63s^23p^63d^44s^1$

13. Point out the particles with the same electronic configurations:

(a) O^{2-} (b) Ne (c) N^{+5} (d) Cl^{+7}

14. How many electrons are situated in the third electron shell of Co?

(a) 15 (b) 2 (c) 7 (d) 8

15. The electronic configuration of Helium atom is $1s^22s^1$:

(a) in its ground state;

(b) in the first excited state;

(c) in the second excited state;

(d) an atom can’t adopt such a configuration.

Answers «Electronic Structure of Atoms»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a	c	b	d	b, c	d	a	a, d	a	b	c	b	a, b, d	a	d

14. THE CHEMICAL BOND

1. What molecules contain only sigma-bonds?

(a) CO_2; (b) NH_3;
(c) H_2O; (d) H_2O_2.

2. Specify the names of substances with predominantly ionic bonding:

(a) sodium chloride; (b) ozone;
(c) hydrogen chloride; (d) calcium fluoride.

3. What types of orbital are overlapped when HCl molecule is formed?

(a) p and p; (b) s and p; (c) s and s; (d) d and p

4. Describe the structure and chemical bonding in the ammonium cation:

(a) the covalent number of nitrogen atom is four 4;
(b) the oxidation state of nitrogen atom is (-4);
(c) the total number of electrons in the cation is ten;
(d) one of the N-H bonds is formed by the donor-acceptor mechanism.

5. Carbon dioxide molecule (CO_2) is nonpolar never the less it contains polar covalent C-O bonds. Give reason for this statement.

(a) Carbon dioxide molecule is nonpolar because it exhibits the bent conformation.

(b) Carbon dioxide molecule is nonpolar because it exhibits the linear conformation.

(c) Carbon dioxide molecule is nonpolar because its overall dipole moment is greater than zero.

(d) Carbon dioxide molecule is nonpolar because its overall dipole moment is zero.

6. What molecule contains the most polar covalent bond?

(a) NH_3; (b) H_2O; (c) HF; (d) HCl.

7. For what atoms (the symbols are given below) the highest covalent number equals to four?

(a) C; (b) N; (c) P; (d) Cl.

8. Hybridization of atomic orbitals is:

(a) the process of mixing the atomic orbitals in an atom to generate a set of new atomic orbitals with different spatial distributions;

(b) the process of molecular orbitals formation;

(c) the process of atomic orbitals overlap;

(d) the changing of the principal quantum number of orbitals.

9. The bond angle H-B-H in BH_3 is equal to 120°. What type of hybridization of the boron orbitals is used to explain the structure of BH_3 molecule?

(a) sp^2; (b) sp; (c) sp^3; (d) dsp^2.

10. What molecules or ions (the formulas are given below) contain covalent bonds formed by the donor-acceptor mechanism?

(a) CO; (b) NH_4^+; (c) H_3O^+; (d) H_2S.

11. Point out the molecules that contain triple bonds:

(a) CO; (b) N_2; (c) O_2; (d) Br_2.

12. Examine energy-level diagrams of H_2, N_2, O_2 and F_2 and indicate paramagnetic molecule:

(a) N_2; (b) H_2; (c) O_2; (d) F_2.

13. Mark the types of intermolecular forces:

(a) hydrogen bond; (b) covalent bond;
(c) dispersion forces; (d) ion — dipole forces.

14. Which of the following species are capable of hydrogen bonding among themselves?

(a) C_2H_6;(b) HI;(c) KF;(d) CH_3COOH.

15. The molecules of what substances are associated by hydrogen bonds?

(a) water; (b) ammine;
(c) hydrogen fluoride; (d) hydrogen iodide.

Answers «The chemical bond»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
b, c, d	a, d	b	a, c, d	b, d	c	a, b	a	a	a, b, c	a, b	c	a, c, d	d	a, b, c

15. COMPLEX (COORDINATIVE) COMPOUNDS

1. Specify the formulas of complex compounds:

(a) $K_3[Fe(CN)_6]$; (b) $(NH_4)_2SO_4$;
(c) $NaKCl_2$; (d) $[Pt(NH_3)Cl_2]$.

2. Coordination number of a complexing agent is four in the following complex compounds:

(a) $K[BiI_4]$; (b) $[Cu(NH_3)_2(H_2O)_2](NO_3)_2$;
(c) $K_3[AlF_6]$; (d) $(NH_4)_2[Ca(SO_4)_2]$.

3. Coordination number of a complexing agent is six in the following complex compounds:

(a) $K_3[Fe(CN)_6]$; (b) $[PtCl(NH_3)_5]Cl_3$;
(c) $K[AlCl_4]$; (d) $K_3[Co(CN)_6]$.

4. The electric charge of a complex ion is minus two in the following complex compound:

(a) $Na_2[Zn(OH)_4]$; (b) $[Cr(NH_3)_4F_2]Cl$;
(c) $Ca_2[Fe(CN)_6]$; (d) $K_4[Fe(CN)_6]$.

5. The electric charge of complex ions is plus two in the following complex compounds:

(a) $K_2[HgI_4]$; (b) $[Cu(NH_3)_4](NO_3)_2$;
(c) $[Cr(NH_3)_5Cl]Cl_2$; (d) $(NH_4)_2[Sn(OH)_4]$.

6. The oxidation state of complexing agents is plus two in the following complex compounds:

(a) $K_3[FeF_6]$; (b) $Na_3[Al(OH)_6]$;
(c) $K_4[Fe(CN)_6]$; (d) $[Pt(NH_3)_2Cl_2]$.

7. The oxidation state of complexing agents is plus three in the following complex compounds:

(a) $[Cr(NH_3)_4F_2]Cl$; (b) $K_4[Pt(OH)_6]$;
(c) $Na[Ag(CN)_2]$; (d) $Na_3[Fe(CN)_6]$.

8. Specify the formula for potassium hexahydroxoplatinate (IV):

(a) $[Pt(H_2O)_6]Cl_4$; (b) $K[Pt(OH)_5NH_3]$;
(c) $[Pt(NH_3)_2Cl_2]$; (d) $K_2[Pt(OH)_6]$.

9. Specify a systematic name for the complex compound whose formula is $K_4[Fe(CN)_6]$.

(a) potassium hexatiocyanoferrate (III);
(b) potassium hexacyanoferrate (II);
(c) potassium hexacyanoferrate (III);
(d) potassium hexatiocyanoferrate (II).

10. Which of the following compounds is a complex nonelectrolyte?

(a) $Na_3[V(CN)_6]$; (b) $[Cr(NH_3)_3Cl]$;
(c) $[Cr(NH_3)_6]Cl_3$; (d) $Na[AgCl_2]$.

11. How many moles of ions are formed by the primary dissociation of 1 mol of dichlorotetraaquachromium (III) nitrate?

(a) 2; (b) 4; (c) 6; (d) 8.

12. How many moles of ions are formed by the primary dissociation of 1 mol of potassium tetracyanodiamminecobaltate(III)?

(a) 2; (b) 3; (c) 4; (d) 5.

13. A solution of $[Co(NH_3)_4SO_4]Cl$ is treated with a small amount of silver nitrate. What substance is precipitated?

(a) $Ag[Co(NH_3)_4SO_4]$; (b) $AgCl$;
(c) Ag_2SO_4; (d) $[Co(NH_3)_4SO_4]NO_3$.

14. Specify the solution with the maximum concentration of copper cations. Assume the identical molarity of complex compounds in their solutions.

(a) $Al[Cu(CN)_4] K_{ins} = 5.13\times 10^{-31}$;
(b) $Na[Cu(CN)_2] K_{ins} = 1.0\times10^{-24}$;
(c) $[Cu(NH_3)_3](NO_3)_2 K_{ins} = 9.33 \times10^{-13}$;
(d) $[Cu(NH_3)_4](NO_3)_2 K_{ins} = 2.89 \times10^{-11}$.

15. Concerning a coordinated complex, which of the following statements **IS NOT** true?

(a) The coordination number is a function of the charge on the metal ion involved.

(b) Some coordinated complexes use metal ions which are not transition-metal ions.

(c) The coordination number is the number of individual species involved in the coordination.

(d) The coordination number is a function of the specific metal ion involved.

Answers «Complex (coordinative) compounds»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, d	a, b, d	a, b, d	a	b, c	c, d	a, d	d	b	b	a	a	b	d	c

16. CHEMISTRY OF THE BIOESSENTIAL ELEMENTS

s-*BLOCK ELEMENTS*

1. Electronic configuration for calcium cation Ca^{2+} in its ground state is:

(a) $1s^22s^22p^63s^23p^6$; (b) $1s^22s^22p^63s^23p^63d^64s^2$
(c) $1s^22s^22p^63s^23p^63d^64s^4$; (d) $1s^22s^22p^63s^23p^63d^64s^1$

2. What reactions prove the basic properties of NaOH?

(a) $NaOH + HCl \rightarrow$; (b) $NaOH + NaHCO_3 \rightarrow$;
(c) $NaOH + N_2O_5 \rightarrow$; (d) $NaOH + FeCl_3 \rightarrow$.

3. Amphoteric hydroxides may be dissolved in:

(a) water,(b) strong acids,
(c) weak acids,(d) alkali solutions.

4. Alkali metals interact with water with the formation of:

(a) hydrides and oxygen gas;
(b) alkalis and hydrogen gas;

(c) peroxides and hydrogen gas;
(d) super oxides and ozone.

5. All s-block metals (except beryllium) interact with hydrogen gas with the formation of

(a) hydroxides; (b) molecular hydrides;
(c) metallic hydrides; (d) saline hydrides.

6. What salts undergo hydrolysis in water solutions?

(a) KF; (b) $Mg(NO_3)_2$; (c) $LiNO_3$; (d) Na_3PO_4.

7. Four s-block metals are essential to life. They are:

(a) sodium, beryllium, cesium and strontium;
(b) potassium, sodium, calcium and magnesium;
(c) sodium, barium, helium and francium;
(d) magnesium, calcium, rubidium and radium.

8. What is the formula of a bone tissue?

(a) $Ca_3(PO_4)_2$; (b) $Ca_5(PO_4)_3F$;
(c) $Ca_5(PO_4)_3OH$; (d) $CaHPO_4$.

9. What are biological functions of sodium in a human body?

(a) maintains fluid balance;
(b) initiates muscle contraction;
(c) prevents ^{137}Cs accumulation;
(d) participates in blood clotting.

10. What medicines are used to decrease acidity of a gastric juice?

(a) MgO; (b) $BaSO_4$;
(c) $NaHCO_3$; (d) $Na_2B_4O_7$.

11. What are biological functions of magnesium in a human body?

(a) Activates protein synthesis.
(b) Prevents ^{90}Sr accumulation.
(c) Activates enzymatic reactions.
(d) Takes part in nerves transitions.

12. What is the formula of a teeth tissue?

(a) $Ca_3(PO_4)_2F$; (b) $Ca_5(PO_4)_3F$;
(c) $Ca_5(PO_4)_3OH$; (d) $CaHPO_4F$

13. What reagent would you employ to determine $\mathbf{Ca^{2+}}$ in a test solution?

(a) Na_2CO_3; (b) $(NH_4)_2C_2O_4$;
(c) $K_2Cr_2O_7$; (d) NaOH.

14. What reagents would you employ to determine **K^+** cation?
(a) $Na_3[Co(NO_2)_6]$; (b) Na_2HPO_4;
(c) $NaHC_4H_4O_6$; (d) $K_2Cr_2O_7$.

15. What reagents would you employ to determine **Mg^{+2}** cation?
(a) $(NH_4)_2CO_3$; (b) $K_2Cr_2O_7$
(c) HPO_4^{2-} and NH_4OH; (d) CH_3COOH

Answers «s-Block elements»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a	a, b, c	b, c, d	b	d	a, b, d	b	c	a, b, c	a, c	a, c, d	b	b	a, c	a, c

p-BLOCK ELEMENTS

1. Mark the correct statements:

(a) in periods from left to the right there is a decrease in atomic radii and increase in ionization potentials of atoms;

(b) in periods from left to the right there is a decrease in electronegativity and electron affinity of atoms;

(c) in groups from top to bottom there is an increase in atomic radii and decrease in ionization potentials of atoms;

(d) in groups from top to bottom there is an increase in electronegativity and electron affinity of atoms.

2. In which of the following serious atoms are arranged in order of decreasing radii?
(a) N, P, As; (b) Al, Si, P;
(c) Br, Cl, F; (d) F, O, N.

3. Non-metallic properties of p-block elements show the certain regularity:
(a) they decrease in periods from left to the right;
(b) they increase in periods from left to the right;
(c) they decrease in groups from top to bottom;
(d) they increase in groups from top to bottom.

4. Point the series that contain only strong acids:
(a) H_2SiO_3, H_2CO_3, CH_3COOH; (b) H_3PO_4, CH_3COOH, HF;
(c) H_2SO_3, HNO_3, HF; (d) HI, H_2SO_4, HNO_3

5. Mark a serious in which the first acid is stronger than the second:
(a) HNO_2 and HNO_3; (b) HNO_3 and H_3PO_4;
(c) H_2SiO_3 and H_2CO_3; (d) $HClO_2$ and $HClO_4$.

6. Mark a serious in which the first base is stronger than the second:
(a) $Al(OH)_3$ and $Mg(OH)_2$; (b) $Mg(OH)_2$ and LiOH;
(c) $Ba(OH)_2$ and $Be(OH)_2$; (d) NaOH and KOH

7. Specify the formula of a hormone gas in a human body which regulates nerve impulse transmitting in brains, macrophages activation and male potency:
(a) NO_2; (b) NO;
(c) N_2O; (d) NH_3.

8. This micro element acts on the nervous system and has calming effect. It counteracts insomnia and relieves pain. It can be useful in treating various nervous disorders. Specify this element:
(a) Ag; (b) Se; (c) Br; (d) I.

9. This chemical element plays an important, yet not fully understood, role in human body. Up to 60 % of it is located in the thyroid gland, producing hormone thyroxin. Specify this element:
(a) Na; (b) I; (c) Fe; (d) S.

10. Specify a gas which is applied in anesthesiology:
(a) NO_2; (b) NO; (c) N_2O; (d) NH_3.

11. What reagent would you employ to determine **I^-** anion?
(a) $Pb(CH_3COO)_2$; (b) Na_2HPO_4;
(c) CH_3COONa; (d) Na_2CO_3.

12. What reagents would you employ to determine **NO_2^-** anion?
(a) concentrated H_2SO_4 solution; (b) $FeCl_3$;
(c) concentrated HNO_3 solution; (d) $KMnO_4$.

13. What reagent(s) would you employ to determine **Br^-** anion?
(a) $AgNO_3$; (b) Na_2HPO_4;
(c) CH_3COONa; (d) Na_2CO_3.

14. What reagent would you employ to determine **Al^{3+}** cation?
(a) H_2SO_4; (b) $K_3[Fe(CN)_6]$;
(c) $K_4[Fe(CN)_6]$; (d) NaOH.

15. What reagent would you employ to determine **SO_4^{2-}** anion?
(a) K_2SO_4; (b) $Na_3PO_4]$;
(c) $K_3[Fe(CN)_6]$; (d) $BaCl_2$

Answers «p-Block elements»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, c	b, c	b, c	d	b	c	b	c	b	c	a	a, d	a	d	d

d-*BLOCK ELEMENTS*

1. The d-block elements exhibit the following electronic configurations:
(a) $ns^2 (n-1) d^x$; (b) $ns^1 (n-1) d^x$;
(c) $ns^2 nd^x$; (d) $ns^1 n d^x$.

2. Electronic configuration of chromium atom is:
(a) $1s^22s^22p^63s^23p^64s^13d^5$; (b) $1s^22s^22p^63s^23p^64s^23d^6$;
(c) $1s^22s^22p^63s^23p^64s^13d^{10}$; (d) $1s^22s^22p^63s^23p^64s^23d^9$.

3. Electronic configuration of Fe^{2+} cation is:
(a) $1s^22s^22p^63s^23p^63d^5$; (b) $1s^22s^22p^63s^23p^63d^6$;
(c) $1s^22s^22p^63s^23p^63d^44s^2$; (d) $1s^22s^22p^63s^23p^63d^54s^1$.

4. The peculiarity of d-block elements is the lack of monotonic alteration in their atomic radii in periods and groups. Give reason for this phenomenon:
(a) the effect of f-compression; (b) the effect of p-compression;
(c) the effect of s-compression; (d) the effect of d-compression.

5. Three elements of the fourth period (iron, cobalt and nickel) form the iron triad. They exhibit similar physical, chemical and biological properties. Give a reason for this similarity:
(a) they have identical electronic structure of their outer layers;
(b) they are d-block elements;
(c) they have close values of their atomic radii and other atomic characteristics;
(d) they are the fourth period elements.

6. d-Block elements are the best complexing agents because:
(a) they are characterized by small ionic radii;
(b) they have relatively high oxidation states;
(c) they are strong reducing agents;
(d) their cations are strong oxidizing agents.

7. Specify the rows that contain only bioessential d-block elements:
(a) Mn, Fe, Ca; (b) Pb, Zn, Cr;
(c) Zn, Al, Fe; (d) Co, Zn, Mn.

8. In a series of hydroxides $Cr(OH)_2 \rightarrow Cr(OH)_3 \rightarrow H_2CrO_4$ their acid-base properties:
(a) do not change; (b) there is increase in acidity;
(c) there is increase in basicity; (d) $Cr(OH)_3$ exhibits acid-base duality.

9. This d-block element is a part of vitamin **B_{12}** which deficiency can cause permanent damage to nervous tissue and pernicious anemia. Specify this element:
(a) Zn; (b) Cu; (c) Co; (d) Hg.

10. This d-block element is an important component of hemoglobin and some enzymes (cytochrom C and others). It takes part in respiration and other metabolic processes. Its deficiency may cause anemia. Specify this element:

(a) Cu; (b) Co; (c) Fe; (d) Cr.

11. This d-block element is poisonous, even in trace amounts. It damages kidneys, lungs, deforms bones, and may cause various cancers. It can also destroy bacteria, fungi and molds. Specify this element:

(a) Au; (b) Co; (c) Mn; (d) Cd.

12. What reagents would you employ to determine $\mathbf{Fe^{3+}}$ cation?

(a) NH_4CNS; (b) $K_4[Fe(CN)_6]$;

(c) $K_3[Fe(CN)_6]$; (d) H_2SO_4.

13. What reagents would you employ to determine $\mathbf{Fe^{2+}}$ cation?

(a) NaOH; (b) $K_4[Fe(CN)_6]$;

(c) $K_3[Fe(CN)_6]$; (d) CH_3COONa.

14. What reagent would you employ to determine $\mathbf{Cu^{2+}}$ cation?

(a) H_2O_2; (b) NaOH;

(c) KI(d) $(NH_4)_2SO_4$ and NH_4OH.

15. What reagents would you employ to determine $\mathbf{Zn^{2+}}$ cation?

(a) H_2SO_4; (b) $K_3[Fe(CN)_6]$;

(c) $K_4[Fe(CN)_6]$; (d) NaOH.

Answers «d-Block elements»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, b	a	b	d	c	a, b	d	b, d	c	c	d	a, b	a, c	d	c, d

17. SURFACE PHENOMENA. ADSORPTION.

1. Specify surface phenomena:

(a) sedimentation,(b) adhesion,

(c) diffusion, (d) cohesion,

2. Specify the formula for the calculation of specific surface area of solid sorbents:

(a) Gs = σ × S; (b) $\sigma = \frac{G_s}{S}$;

(c) $S = \frac{1}{\Gamma_{\max} \times N_A}$; (d) $a_s = \frac{A_s}{m}$.

3. Point out the correct statements:

(a) adsorption is the attachment of particles of an adsorbate to the surface of adsorbents;

(b) physical adsorption is reversible and exothermic;

(c) physical adsorption is irreversible and endothermic;

(d) chemisorption is an irreversible process.

4. Molecular adsorption is the adsorption of non electrolytes or weak electrolytes from gaseous and liquid phases at solid sorbents. It is described by:

(a) the Langmuir adsorption isotherm;

(b) the Freundlich adsorption isotherm;

(c) the BET adsorption isotherm;

(d) the Gibbs adsorption isotherm.

5. Surfactants (surface active agents) are substances that:

(a) reduce surface tension of water;

(b) increase surface tension of water;

(c) do not change surface tension of water,

(d) reduce polarity of medium.

6. Specify a series that contains surfactants only:

(a) formic acid, acetic acid, propionic acid;

(b) acetic acid, propionic acid, valeric acid;

(c) sodium carbonate, glucose, formic acid;

(d) glucose, acetic acid, benzene.

7. What factors decrease surface tension of water?

(a) Dissolving of fatty carboxylic acids.

(b) Dissolving of alcohols.

(c) Increase in temperature.

(d) Decrease in temperature.

8. Surface activity of carboxylic acids depends upon their:

(a) ionization percent in water solutions;

(b) acidity (pH);

(c) osmotic pressure;

(d) number of CH_2 groups in radicals.

9. Surfactants are applied:

(a) as soaps and detergents; (b) as antiseptics in surgery;

(c) for liposome productions; (d) for isotonic solutions productions.

10. Traube’s Rule postulates that surface tension of the organic compounds belonging to the homological series of R $(CH_2)_n$ X shows certain regularity:

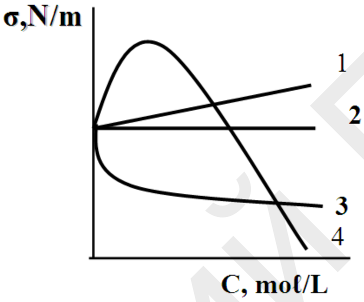
(a) for each additional CH_2 group the concentration required to give a certain surface tension was reduced by factor 3.0;

(b) for each additional CH_2 group the concentration required to give a certain surface tension was reduced by factor 3.5;

(c) for each additional CH_2 group the concentration required to give a certain surface tension was reduced by factor 2.5;

(d) for each additional CH_2 group the concentration required to give a certain surface tension was increased by factor 4.0.

11. What curve shows the dependence of the surface tension of the aqueous solution from acetic acid concentration?



(a) 1; (b) 2; (c) 3; (d) 4.

12. Name the types of electrolytes’ adsorption at solid sorbents:

(a) molecular adsorption; (b) selective adsorption;

(c) ion-exchange adsorption; (d) distributive adsorption.

13. Specify the Langmuir equation:

(a) $\Gamma = \Gamma_{max}\frac{P}{P + a}$ (b) $æ = k \times p^{1/n}$;

(c) $\Gamma = \frac{a}{RT} \times \frac{bC_M}{1 + bC_M}$ (d) $\sigma = \sigma_0 - \alpha \times \ln(1 + b \times C_{sur})$

14. What ions predominantly adsorb from aqueous solution on the surface of crystalline AgI?

(a) K^+; (b) I^-; (c) Ag^+; (d) NO_3^-.

15. Specify the important characteristics of the ion exchange adsorption:

(a) in the adsorption process loosely held ions at fixed-charged sites on solids are exchanged with charged ions that are dissolved in solutions;

(b) solid sorbents capable of ion exchange, are called ionites or ionic exchangers;

(c) each active site of a sorbent adsorbs only one adsorbate molecule;
(d) solid surface is not uniform.

Answers «Surface phenomena. Adsorption»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
b, d	d	a, b, d	a, b, c	a, d	d	a, b, c	d	a, b, c	a, b	c	b, c	a	b, c	a, b

18. COLLOIDAL CHEMISTRY

1. Specify the correct statements:
(a) a colloidal solution can be prepared by NaCl dissolution in water;
(b) a dispersed system is a micro heterogeneous system in which fine particles of a dispersed phase are distributed in a dispersion medium;
(c) a colloidal solution is a single-phase system of variable composition;
(d) a colloidal solution is thermodynamically unstable.

2. Specify liquid aerosols:
(a) fog; (b) smoke;
(c) liquid sprays; (d) milk.

3. Specify emulsions:
(a) pearl; (b) toothpaste;
(c) milk; (d) mayonnaise

4. Specify the correct statements:
(a) lyophilic sols are stable due to solvation;
(b) lyophobic sols are unstable because they are not solvated;
(c) lyophobic sols are stabilized by electrolytes;
(d) lyophobic sols are formed spontaneously.

5. Which of the following systems are bind dispersed?
(a) powders; (b) foams;
(c) gels; (d) jelly.

6. Specify the methods of dispersed systems preparing:
(a) peptization;(b) degradation of bulk matter;
(c) ultra filtration(d) condensation.

7. The methods of dispersed systems purification are:
(a) dialysis; (b) degradation of bulk matter;
(c) ultrafiltration; (d) condensation.

8. Electrophoresis is defined as:
(a) an electrical transfer of dispersed particles;
(b) an electrical transfer of dispersion medium through semipermeable membrane;

(c) a formation of solvates or hydrates complexes;
(d) a reversible thermodynamic process of water diffusion through semipermeable membrane from pure water to a solution.

9. Name the special optical properties of colloidal solutions:
(a) light absorption;(b) light scattering;
(c) light reflection; (d) light refraction.

10. Coagulation is defined as:
(a) sedimentation of dispersed particles under the effect of gravity;
(b) swelling of dispersed particles;
(c) shrinking of colloidal particles;
(d) irreversible aggregation of dispersed particles into large particles followed by rapid precipitation.

11. Identify the factors of aggregative stability of sols.
(a) Brownian motion;
(b) temperature;
(c) the degree of dispersion;
(d) the presence of foreign substances in the solution (electrolyte or polymers).

12. Name specific physical properties of sols:
(a) diffusion; (b) sedimentation;
(c) crystallization; (d) light scattering.

13. Electrokinetic (ξ)-potential characterizes:
(a) stability of colloidal solutions;
(b) the electrophoretic mobility of dispersed particles;
(c) the electric charge of dispersed particles;
(d) the rate of colloidal particles sedimentation.

14. Barium sulfate sol was prepared according to the reaction

$$H_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2\ HCl$$

Assume $BaCl_2$ was the excess and specify the correct formula of a micelle:
(a) $\{[mBaSO_4]\ n\ SO_4^{-2}, 2(n-x)\ H^+\}\ 2xH^+$;
(b) $\{[mBaSO_4]\ n\ Ba^{+2}, n\ SO_4^{2-}\}\ 2xSO_4^{2-}$;
(c) $\{[mBaSO_4]\ n\ Ba^{+2}, 2(n-x)\ Cl^-\}\ 2xCl^-$;
(d) $\{[mBaSO_4]\ n\ Ba^{+2}, (n-x)\ Cl^-\}\ xCl^-$.

15. Zinc sulfide sol was prepared according to the reaction:

$$H_2S + ZnCl_2 \rightarrow ZnS + 2\ HCl$$

Assume H_2S was the excess and answer the following questions:

A. What ions are potential determining (PDI) in a prepared colloidal particle?
(a) Zn^{2+}; (b) H^+; (c) Cl^-; (d) HS^-.

B. What ions form the adsorption layer in a prepared colloidal particle?
(a) Zn^{2+}; (b) H^+; (c) Cl^-; (d) HS^-.

C. What is the charge of a nucleus in a prepared colloidal particle?
(a) positive; (b) zero; (c) negative.

D. What is the charge of the colloidal particle in a prepared sol?
(a) positive; (b) zero; (c) negative.

E. Specify the ions of diffusion layer in a prepared colloidal particle?
(a) Zn^{2+}; (b) H^+; (c) Cl^-; (d) HS^-.

F. What ions can initiate the coagulation process in the prepared sol?
(a) Zn^{2+}; (b) H^+; (c) Cl^-; (d) HS^-.

Answers «Colloidal Chemistry»

1	2	3	4	5	6	7	8	9	10	11	12	13	14
d	a, c	c, d	a, b, c	c, d	a, b, d	a, c	a	b	d	d	a, b, d	a, b	c

15 A	15 B	15 C	15 D	15 E	15 F
b, d	b, d	c	c	b	a, b

19. MACROMOLECULES AND THEIR SOLUTIONS

1. Indicate, which macromolecules given below, belong to synthetic polymers:
(a) polyethylene terephthalate; (b) cellulose;
(c) proteins; (d) polyisoprene.

2. Indicate, which macromolecules given below, belong to biopolymers:
(a) starch; (b) glycogen;
(c) vulcanized rubber; (d) proteins.

3. Indicate. which macromolecules given below, belong to polyelectrolytes:
(a) cellulose; (b) glycogen;
(c) nucleic acids; (d) proteins.

4. Indicate, which macromolecules given below, belong to amphiprotic polyelectrolytes:
(a) starch; (b) glycogen;
(c) vulcanized rubber; (d) proteins

5. Mark the correct statements:

(a) isoelectric point (pI) is the pH at which the net charge on a macromolecule is zero;

(b) electrophoresis is the migration of charged molecules in a solution in response to an electric field;

(c) salting-out effect is the increase in solubility under the influence of electrolytes;
(d) salting-in effect is the decrease in solubility under the influence of electrolytes.

6. Mark the correct statements:
(a) polymers form both true and colloidal solutions;
(b) limited swelling results in formation of true solutions;
(c) unlimited swelling results in gels formation
(d) polyelectrolytes contain both acidic and basic ionizable groups

7. The specific properties of polymers are:
(a) flexibility of macromolecules; (b) strong intermolecular forces;
(c) swelling; (d) diffusion.

8. Swelling is a spontaneous irreversible diffusion of solvent molecules into a polymer phase. It is affected by the following factors:
(a) nature of a high-molecular compounds and nature of a solvents;
(b) configuration of chains;
(c) acidity of a medium (for amphiprotic polyelectrolytes only);
(d) temperature.

9. In what solvent gelatin does exhibit the highest swelling percent?
(a) water; (b) alcohol;
(c) benzene; (d) toluene.

10. Specify the properties that are common for both colloidal solutions, and solutions of high-molecular compounds:
(a) the solutions are stable due to solvation;
(b) the solutions are formed spontaneously;
(c) the solutions are able to swell;
(d) light scattering.

11. The specific physical properties of proteins at isoelectric state are:
(a) minimum swelling percent; (b) maximum coagulation percent;
(c) zero electrophoretic mobility; (d) maximum solubility in water.

12. The isoelectric point of muscle myosin is 5. Its swelling per cent is minimum at pH:
(a) 2; (b) 4; (c) 5; (d) 7.

13. Isoelectric point of albumin is 4.8. Albumin was dissolved in a buffer solution with pH = 7. Towards what electrode protein molecules will migrate in the electric field?
(a) towards cathode;
(b) towards anode;
(c) don’t migrate.

14. Isoelectric points of protein A and protein B are equal to 5 and 8 correspondently. In what pH range they can be separated by electrophoresis?

(a) from 5 to 8;
(b) from 5 to 7;
(c) from 7 to 8;
(d) from 3 to 5.

15. Protected lyophobic colloids are:

(a) colloidally stable mixture of a lyophobic and lyophilic colloids;
(b) colloidally stable mixture of a lyophobic colloids and proteins;
(c) colloidally stable mixture of a lyophobic colloids and salts;
(d) colloidally stable mixture of a lyophobic colloids and alkali hydroxides.

Answers «Macromolecules and their solutions»

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
a, d	a, b, d	c, d	d	a, b	a, d	a, b, c	a, b, c, d	a	d	a, b, c	c	b	a	a, b

Appendix 2

Table 1 — The instability constants

Complex ion	K_{ins}	Complex ion	K_{ins}
$[Ag(CN)_2]^-$	1.41×10^{-20}	$[CdI_4]^{2-}$	7.9×10^{-7}
$[Ag(NH_3)_2]^+$	5.75×10^{-8}	$[Cd(CN)_4]^{2-}$	7.76×10^{-18}
$[Ag(NO_2)_2]^-$	1.48×10^{-3}	$[Cu(NH_3)_4]^{2+}$	9.33×10^{-13}
$[Ag(NCS)_2]^-$	5.37×10^{-9}	$[Cu(NCS)_4]^{2-}$	3.02×10^{-7}
$[Ag(S_2O_3)_2]^{3-}$	3.47×10^{-14}	$[Co(NH_3)_4]^{2+}$	4.07×10^{-5}
$[Au(CN)_2]^-$	5.0×10^{-39}	$[Co(NH_3)_6]^{2+}$	8.51×10^{-6}
$[Bi(NCS)_6]^{3-}$	5.89×10^{-5}	$[Co(CN)_6]^{4-}$	8.13×10^{-20}
$[Cd(NH_3)_4]^{2-}$	2.88×10^{-7}	$[Co(NCS)_4]^{2-}$	6.31×10^{-3}
$[CdBr_4]^{2-}$	1.17×10^{-3}	$[Co(NH_3)_6]^{3+}$	6.17×10^{-36}
$[Co(CN)_6]^{3-}$	1.0×10^{-64}	$[PbBr_4]^{2-}$	1.0×10^{-3}
$[Cr(NCS)_6]^{3-}$	1.58×10^{-4}	$[PbI_4]^{2-}$	6.0×10^{-7}
$[Fe(CN)_6]^{4-}$	1.0×10^{-24}	$[Pb(NCS)_4]^{2-}$	0.14
$[Fe(CN)_6]^{3-}$	1.0×10^{-31}	$[Pb(S_2O_3)_4]^{6-}$	6.31×10^{-8}
$[Fe(NCS)_6]^{3-}$	5.89×10^{-4}	$[PbCl_4]^{2-}$	0.1
$[HgBr_4]^{2-}$	1.0×10^{-21}	$[PbBr_4]^{2-}$	7.9×10^{-14}
$[Hg(CN)_4]^{2-}$	3.1×10^{-42}	$[PtCl_4]^{2-}$	1.0×10^{-16}
$[HgCl_4]^{2-}$	8.5×10^{-16}	$[PtBr_4]^{2-}$	3.0×10^{-21}
$[Hg(NH_3)_4]^{2-}$	5.0×10^{-20}	$[Zn(NH_3)_4]^{2+}$	2.0×10^{-9}
$[HgI_4]^{2-}$	0.51×10^{-30}	$[ZnCl_4]^{2-}$	10
$[Hg(NCS)_4]^{2-}$	1.7×10^{-20}	$[ZnBr_4]^{2-}$	316.2
$[Mn(C_2O_4)_3]^{3-}$	3.8×10^{-20}	$[Zn(CN)_4]^{2-}$	1.0×10^{-19}
$[Ni(NH_3)_4]^{2+}$	3.4×10^{-8}	$[Zn(NCS)_4]^{2-}$	2.0×10^{-4}

Table 2 — Surface tension of some liquids at different temperature

Substances	283 K	293 K	298 K	303 K
Benzol	30.24×10^{-3}	28.88×10^{-3}	28.18×10^{-3}	27.49×10^{-3}
Water	74.22×10^{-3}	72.75×10^{-3}	71.96×10^{-3}	71.15×10^{-3}
Acetic acid	28.80×10^{-3}	27.80×10^{-3}	—	26.80×10^{-3}
Pentane	17.10×10^{-3}	16.00×10^{-3}	15.48×10^{-3}	14.95×10^{-3}
Ethanol	23.14×10^{-3}	22.03×10^{-3}	—	21.45×10^{-3}

Table 3 — Content in a human body of bioessential chemical elements

Elements	Content in a human body per 70 kg	Percent by mass
Na	100 g	0.14%
K	140 g	0.2%
Mg	19 g	0.027%
Ca	1000 g	1.4%
C	16 kg	22.8%
N	1.8 kg	2.6 %
O	43 kg	61.5%
P	780 g	1.1%
S	140 g	0.2%
Cl	95 g	0.14%
Ag	7.9×10^{-4} g	1.1×10^{-6}%
V	0.013g	1.9×10^{-5}%
W	0.013g	1.9×10^{-5}%
Au	9.8×10^{-3} g	1.4×10^{-5}%
Co	1.5×10^{-3} g	2.1×10^{-6}%
Mn	0.012 g	1.7×10^{-5}%
Mo	9.5×10^{-3} g	1.4×10^{-5}%
Cd	0.05 g	4.1×10^{-5}kg
Cu	0.072 g	1.0×10^{-4}%
Zn	2.3 g	3.3×10^{-3}%
Fe	4.2 g	6.0×10^{-3}%

Table 4 — Bioessential elements in the periodic table

IA	IIA											IIA	IVA	VA	VIA	VIIA	VIIIA
H																	He
Li	Be											*B*	C	N	O	*F*	Ne
Na	**Mg**	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	*Al*	*Si*	P	S	**Cl**	Ar
K	**Ca**	Sc	Ti	V*	*Cr*☆	*Mn*	*Fe*	*Co*☆	*Ni*☆	*Cu*	*Zn*	Ga	Ge	As*	*Se*	*Br*	Kr
Rb	Sr	Y	Zr	Nb	*Mo*	Tc	Ru	Rh	Pd	Ag	Cd*	In	Sn	Sb	Ne	*I*	Xe
Cs	Ba*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg*	Tl	Pb*	Bi	Po	At	Rn
Fr	Ra*	Ac	Rf	Db	Sg	Bh	Hs	Mt									

X — Bioessential elements (are contained in biomass)
X — Biometals (metals of life)
X — Macro elements
X — Microelements
***** — Extremely toxic metals

Table 5 — Biological functions of alkali metals. Application of their compounds in medicine

Element	Content in a human body	Topography in a human body	Biological functions	Some medicines containing these metals
Na	100g/70kg of a body mass or 0.14 %	Presents in all tissues, intracellular and extracellular fluids	Sodium holds water in body tissues. Adjust acid-base balance. Involved in nerve impulse transmission. Maintains osmotic pressure. Excessive intake of sodium may cause a hypertension. Recommended intake is 2,400–3,000 mg /day	0.9% NaCl solution — plasma substituents (isotonic solution), 10 % NaCl solution — to cure purulent wounds, $NaHCO_3$ (sodium bicarbonate) – antacidic drug: $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ $Na_2B_4O_7 \times 10H_2O$(borax) — for disinfection, $NaNO_2$ — to treat heart diseases
K	140g/70 kg of a body mass or 0.2 %	Presents in all tissues, intracellular and extracellular fluids	Potassium acts at cell membranes in transmitting electrochemical impulses in nerve and muscle fibers. Act in balancing the activity of food intake and waste removal from cells. Is involved in protein synthesis, fluid balance, and muscle contraction. Prevent ^{137}Cs accumulation. K deficiency causes weakness, mental confusion, and possible death. Excessive intake causes weakness and possible vomiting. Estimated minimum requirements are 2,000 mg/day.	KCl — to maintain electrolyte balance KI — to protect against iodine deficiency and to treat endemic goiter myxedema.

Element	Content in a human body	Topography in a human body	Biological functions	Some medicines containing these metals
H	7 kg/ 70 kg of a body mass or 10%	Presents in all tissues, intracellular and extracellular fluids.	Hydrogen ions (H^+) effect the pH of different body fluids. Hydrogen in the cells is responsible to eliminate wastes from the body. Hydrogen strengths and body's immune system and thus send defensive cells to fight of infection-causing fungus, bacteria and viruses. Hydrogen ions (H^+)activate enzymes; they are involved in proteins, polysaccharides and lipids hydrolysis. Water is the medium for biochemical reactions running.	H_2O_2 (3%) — an antiseptics; H_2O_2 (30%) — treatment of warts and warty form of lichen planus; Heavy water — to study the rate of water absorption in a body; Deuterium (D) — for studying pharmacokinetics of medicines; Tritium (T) — for studying metabolic processes and the total amount of water in a body. $NaHCO_3$ an antacid drug

Table 6 — Biological functions of alkaline earth metals. Application of their compounds in medcine

Element	Content in a human body	Topography in a human body	Biological functions	Some medicines containing these metals
Mg	19g/70kg of a body mass or 0.027%	Presents in intracellular and extracellular fluids, in bone tissue, and in muscles. Magnesium is also present in the green plant pigment chlorophyll.	Magnesium is involved in bones' mineralization and protein synthesis. It activates enzymatic reactions and takes part in nerves transitions. Symptoms of magnesium deficiency are weakness, confusion, hypertension, arrythmia, depressed pancreatic hormone secretion, growth failure, behavioral disturbance, and muscle spasms. Recommended intakes for adults 280–350 mg/day.	$MgSO_4 \cdot 7H_2O$ is used to control seizures in pregnancy, to treat low magnesium levels and problems related to kidney conditions (nephritis) in children. This drug is also used for preventing premature contractions in pregnancy and to treat heart attack and asthma patients. MgO is an antacid to relieve heartburn, sour stomach, or acid indigestion. Magnesium oxide also may be used as a laxative for short-term, rapid emptying of the bowel (before surgery, for example). Magnesium oxide also is used as a dietary supplement when the amount of magnesium in the diet is not enough. $Mg(OH)_2 \cdot 4MgCO_3 \cdot H_2O$-antacidic drug; $MgSiO_3 \cdot nH_2O$-enterosorbent.

Element	Content in a human body	Topography in a human body	Biological functions	Some medicines containing these metals
Ca	1000g/70kg of a body mass or 1.4%	99% of Ca is concentrated in bones as $Ca_5(PO_4)_3OH$ and in teeth as $Ca_5(PO_4)_3F$; 1% of calcium is in blood plasma, muscles, liver, kidneys and other organs where it presents as ions or as complex compounds.	Calcium is the principal skeletal mineral in bones and teeth. It is involved in blood clotting, muscle contraction, nerve transmission, and heart action. Protection of a human body from ^{90}Sr accumulation. Calcium deficiency results in a range of health problems: osteoporosis, stunted childhood growth, hypertension, preeclampsia and colon cancer.	$CaCl_2$ — increases blood clotting. $CaCl_2 \cdot 6H_2O$ is applied to treat allergy. $CaSO_4 \times 2H_2O \times 2CaSO_4 \times H_2O$ (gypsum) is applied in surgical dentistry and surgery. Radioactive isotope ^{45}Ca is used to study metabolic processes in a body; Calcium gluconate, glycerolphosphate and pantetonate are applied for health promotion.
Sr	0.32g/70kg of a body mass or 4.1×10^{-4} %	Strontium is accumulated mainly in bone tissue.	Strontium may incorporate into the bone tissue (especially when there is calcium deficiency in a body). It may cause the disturbance in skeleton calcification and blood production. Radioactive isotope ^{90}Sr is a health hazard when it concentrates in bone surfaces and bone marrow. The health effects associated with strontium-90 are bone tumors and tumors of the blood-cell forming organs.	Radioactive isotopes ^{89}Sr and ^{90}Sr are used in radiation therapy in the treatment of bone tumors.
Ba	0.022g/70kg of a body mass or 3.1×10^{-5} %	Barium is accumulated mainly in retina.		$BaSO_4$ is used to examine the esophagus (tube that connects the mouth and stomach), stomach, and intestine using X-rays or computed tomography (CAT scan, CT scan; a type of body scan that uses a computer to put together X-ray images to create cross-sectional or three dimensional pictures of the inside of the body). Barium sulfate is in a class of medications called radiopaque contrast media. It works by coating the esophagus, stomach, or intestine with a material that is not absorbed into the body so that diseased or damaged areas can be clearly seen by X-ray examination or CT scan.

Table 6 — Biological functions of alkaline earth metals. Application of their compounds in medcine

Element	Content in a human body	Topography in a human body	Biological functions	Some medicines containing these metals
Mg	19g/70kg of a body mass or 0.027%	Presents in intracellular and extracellular fluids, in bone tissue, and in muscles. Magnesium is also present in the green plant pigment chlorophyll.	Magnesium is involved in bones' mineralization and protein synthesis. It activates enzymatic reactions and takes part in nerves transitions. Symptoms of magnesium deficiency are weakness, confusion, hypertension, arrythmia, depressed pancreatic hormone secretion, growth failure, behavioral disturbance, and muscle spasms. Recommended intakes for adults 280–350 mg/day.	$MgSO_4 \cdot 7H_2O$ is used to control seizures in pregnancy, to treat low magnesium levels and problems related to kidney conditions (nephritis) in children. This drug is also used for preventing premature contractions in pregnancy and to treat heart attack and asthma patients. MgO is an antacid to relieve heartburn, sour stomach, or acid indigestion. Magnesium oxide also may be used as a laxative for short-term, rapid emptying of the bowel (before surgery, for example). Magnesium oxide also is used as a dietary supplement when the amount of magnesium in the diet is not enough. $Mg(OH)_2\ 4MgCO_3 \cdot H_2O$-antacidic drug; $MgSiO_3 \cdot nH_2O$-enterosorbent.
Ca	1000g/70kg of a body mass or 1.4%	99% of Ca is concentrated in bones as $Ca_5(PO_4)_3OH$ and in teeth as $Ca_5(PO_4)_3F$; 1% of calcium is in blood plasma, muscles, liver, kidneys and other organs where it presents as ions or as complex compounds.	Calcium is the principal skeletal mineral in bones and teeth. It is involved in blood clotting, muscle contraction, nerve transmission, and heart action. Protection of a human body from ^{90}Sr accumulation. Calcium deficiency results in a range of health problems: osteoporosis, stunted childhood growth, hypertension, preeclampsia and colon cancer.	$CaCl_2$ — increases blood clotting. $CaCl_2 \cdot 6H_2O$ is applied to treat allergy. $CaSO_4 \times 2H_2O \times 2CaSO_4 \times H_2O$ (gypsum) is applied in surgical dentistry and surgery. Radioactive isotope ^{45}Ca is used to study metabolic processes in a body; Calcium gluconate, glycerol-phosphate and pantetonate are applied for health promotion.

Element	**Content in a human body**	**Topography in a human body**	**Biological functions**	**Some medicines containing these metals**
Sr	0.32g/70kg of a body mass or 4.1×10^{-4} %	Strontium is accumulated mainly in bone tissue.	Strontium may incorporate into the bone tissue (especially when there is calcium deficiency in a body). It may cause the disturbance in skeleton calcification and blood production. Radioactive isotope ^{90}Sr is a health hazard when it concentrates in bone surfaces and bone marrow. The health effects associated with strontium-90 are bone tumors and tumors of the blood-cell forming organs.	Radioactive isotopes ^{89}Sr and ^{90}Sr are used in radiation therapy in the treatment of bone tumors.
Ba	0.022g/70kg of a body mass or 3.1×10^{-5} %	Barium is accumulated mainly in retina.		$BaSO_4$ is used to examine the esophagus (tube that connects the mouth and stomach), stomach, and intestine using X-rays or computed tomography (CAT scan, CT scan; a type of body scan that uses a computer to put together X-ray images to create cross-sectional or three dimensional pictures of the inside of the body). Barium sulfate is in a class of medications called radiopaque contrast media. It works by coating the esophagus, stomach, or intestine with a material that is not absorbed into the body so that diseased or damaged areas can be clearly seen by X-ray examination or CT scan.

Table 7 — Biological functions of p-block macro elements. Application of their compounds in medicine.

Element	Content in a human body	Biological functions	Some medicines containing these metals
N	1.8kg/70 kg of a body mass or 2.6 %	Nitrogen is one of the most important bioessential chemical elements. It’s contained in amino acids, proteins, nucleic acids, biological amines and some other bioactive compounds. In 1991 it was revealed that nitrogen monoxide. NO is the only hormone gas in a human body which regulates nerve impulse transmitting in brains, macrophages activation and male potency.	N_2O (laughing gas) is used for anesthesia. NH_3 — for blood vessels broadening and breathing center activation. NH_4Cl is applied as diuretic. $NaNO_2$ — vasodilator vascular spasm of the heart and brain. Glycine — to enhance mental alertness. Nitroglycerin — to normalize the heart action.
C	16 kg/70 kg of a body mass or 22.8%	Carbon is a component of all organic components (proteins, carbohydrates, lipids, hormones, vitamins and others) CO_2 is a final product of metabolic processes. Hydrocarbon buffer system plays important role in acid-base status maintaining. This buffer is contained in all biological fluids. CO getting into the bloodstream forms a stable complex with hemoglobin thus hemoglobin loses its ability to carry oxygen. Coal dust causes a professional disease — anthracosis.	Activated carbon — an adsorbent used in healing heavy metals poisoning. It’s also used as hemosorbent for blood purification; $NaHCO_3$ — antacidic drug of gastric juice; to heal acidosis; CO_2 and O_2 — a mixture containing 5% carbon dioxide and 95% of oxygen is used to activate a breathing center in a human body.
O	43kg/70 kg of a body mass or 61.5%	Oxygen is a component of water and all bioactive molecules. Oxygen gas is the most important oxidizing agent in vivo. The decrease of oxygen content in air may cause death.	A new region of medicine – hyperbaric oxygenation is used for activation of metabolic processes in a human body. Ozone (O_3) is used to disinfect the premises, air disinfection and purification of drinking water; a small admixture of ozone in the air gives a beneficial effect on patients with pulmonary deseases.
P	780g/70 kg of a body mass or 1.1%	Phosphorus is an essential element for plants and animals. Humans and many other creatures need phosphorus to build teeth and bones. All living organisms use it to build their cells and to store and use energy. Phosphorus is a component of ATP, phosphorlipids, and nucleic acids. Phosphate anions are the components of hydro phosphoric buffer system (Na_2HPO_4/NaH_2PO_4) that controls acid-base status of a body.	ATP — to treat chronic coronary artery disease and muscular dystrophy. $AlPO_4$ and $Zn_3(PO_4)_2$ are used in dentistry as a filling material Calcium glycerol phosphate is a source of calcium for the body. Organophosphorus compounds are potent poisons (part of the chemical warfare agents).

Element	Content in a human body	Biological functions	Some medicines containing these metals
S	140g/70 kg of a body mass or 0.2%	Sulfur is necessary to sustain bioactivity of proteins: it kills bacteria, fungi and skin parasites. It can be helpful in treating various cancer, food poisoning, bacterial and fungal diseases, and blood infections. Sulfur prevents the effects of active radicals on nucleic acids and other bio molecules.	$Na_2SO_4\cdot 10H_2O$ — laxative; $CuSO_4\cdot 5H_2O$ and $ZnSO_4\cdot 7H_2O$ — antiseptics. $Na_2S_2O_3\cdot 5H_2O$- anti toxic, anti-inflammatory and desensitizing agent. $BaSO_4$- radiopaque contrast media. $MgSO_4\cdot 7H_2O$ is applied for lowering blood pressure in hypertension; also used as laxative. Purified sulfur is used as a laxative, as well as externally in the form of ointments and powders for the treatment of skin diseases.
Cl	95g/70 kg of a body mass or 0.14%	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: Chlorine is also helpful in fighting cancer.	$CaOCl_2$ — bleach, disinfectant. HCl (8 %) — to increase gastric juice acidity. NaCI (0,9 %) — isotonic solution applied as blood substituents. NaCI (3–5–10 %) — hypertonic solution, used to heal purulent wounds. NaCI (2–5 %) is used for gastric lavage in poisoning by $AgNO_3$.

Table 8 — Biological functions of p-block micro elements. Application of their compounds in medicine

Element	Content in a human body	Biological functions	Some medicines containing these metals
Al	0.061/70 kg of a body mass or 8.7×10^{-5}%	Aluminum neutralizes acids in stomach juices and as such is used to control heartburn and ulcers in gastric tract. It also has antiinflammatory properties.	$KAl(SO_4)_2\cdot 12H_2O$ — have an astringent, styptic and cauterizing action; $Al(OH)_3$ — absorbent and enveloping effect, lowers the acidity of gastric juice, is part of a combined drug «Almagel»; $Al(CHCOO)_3$ — the Burov's liquid (8 % solution) — astringent $Al_2O_3\cdot 2SiO_2\cdot 2H_2O$ — white clay (kaolin) — dentistry (cement, filling material, stamping crowns)
F	2.6/70 kg of a body mass or 3.7×10^{-3}%	Fluorine 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.	NaF is included in toothpaste, is used to prevent tooth decay. Fluoridation of drinking water leads to a decrease in the incidence of dental caries.

Element	Content in a human body	Biological functions	Some medicines containing these metals
Br	0.2/70 kg of a body mass or 2.9×10^{-4}%	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.	NH_4Br, KBr, NaBr — calming effect on the central nervous system.
I	0.013/70 kg of a body mass or 1.9×10^{-5}%	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 thyroxin 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)	Radioactive isotopes are applied for the treatment and diagnostics of the thyroid gland diseases; Alcohol iodine solutions (5- or 10 %) is applied as antiseptics; 5% solution was administered orally for the prevention of atherosclerosis; I_2/KI — Lugol's solution — lubrication of the mucosa of the pharynx and la-rynx; KI and NaI — «Antistrumin» is used in the endemic goitre, as well as expectorants in inflammatory diseases of the respi-ratory tract
Se	0.013/70 kg of a body mass or 1.9×10^{-5} %	Even although its daily intake is only 0.01 mg, selenium is 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	Selenium is a component of antioxidant complex that contains vitamins A, E and C

Table 9 — biological functions of p-block macro elements. Application of their compounds in medicine

Element	Content in a human body	Biological functions	Some medicines containing these metals
Mn	0.012/70 kg of a body mass or 1.7×10^{-5}%	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.	$KMnO_4$ — topical medication that has antimicrobial and cauterizing properties is used for neutralization of toxic organic substances. 5% $KMnO_4$ solution is used as hemostyptic.
Fe	4.2/70 kg of a body mass or 6.0×10^{-3}%	It's an important component of hemoglobin and some enzymes (cytochrom C and others). It takes part in respiration and other metabolic processes. Its deficiency may cause anemia.	$FeCl_2$ and $FeSO_4$ are used for the treatment of iron deficiency anemia, as well as to treat weakness and exhaustion. $FeCl_3$ — cautery, styptic, disinfectant.

Element	Content in a human body	Biological functions	Some medicines containing these metals
Co	1.5×10^{-3} /70 kg of a body mass or 2.1×10^{-6}%	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.	^{60}Co – diagnostics and treatment of malignant tumors. Vitamin B 12 improves the state of the patient with anemia, nervous disorders.
Cu	0.072×10^{-3} /70 kg of a body mass or 1.0×10^{-4}%	It is an important enzymes' activator, which fulfills a catalyst function in a body. It plays an important role in blood formation.	0.25% $CuSO_4 \cdot 5H_2O$ — to treat inflammation of the mucous membranes and conjunctivitis, small doses of the drug — to enhance erythropoiesis in anemia. $(Cu_2C_6H_4O_7)_2 \cdot 5H_2O$ — eye ointment. Some alloys of copper with silver and gold used in dentistry
Zn	2.3/70 kg of a body mass or 3.3×10^{-3}%	It's contained in erythrocytes and takes part in tissues' respiration. Is used in treating leukemia and various cancers, viral and bacterial diseases. It is being tested in treating early stages of AIDS.	$ZnSO_4 \cdot 7H_2O$ — eye drops. ZnO — powders, ointments, pastes for skin diseases. Zinc-insulin — a drug for the treatment of diabetes. $ZnCl_2$ – in dentistry for cauterization of papillomas, for the treatment of inflamed mucous membranes.
Mo	9.5×10^{-3} /70 kg of a body mass or 1.4×10^{-5}%	Is present in human body in trace amounts and role is not totally understood, but its lack may cause diarrhea, changes in sexual glands, tooth decay. It s helpful in fighting inflammations caused by viruses or bacteria and in arteriosclerosis.	Compounds of molybdenum are used for qualitative and quantitative determination of protein in biological objects.
Ag	9.5×10^{-3} /70 kg of a body mass or 1.4×10^{-5}%	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.	$AgNO_3$ (lapis) is used in dentistry for the silver root canals and cavities of the teeth prior to sealing. AgCl — bactericidal action, used to treat mucous membranes of the eye. Protargol (silver protein complex) and collargol (colloidal silver) are used to treat conjunctivitis, infectious diseases of the mucous membranes (nose, throat, etc.)

Element	Content in a human body	Biological functions	Some medicines containing these metals
Au	9.8×10^{-3} /70 kg of a body mass or 1.4×10^{-5} %	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 fighting inflammations. It helps in later stages of any therapy in tissue regeneration.	^{198}Au — treatment of malignant tumors. Some alloys with copper and silver are used in dentistry. Gold threads are used in cosmetics. Monovalent gold compounds are used in chemotherapy.
W	0.013/70 kg of a body mass or 1.9×10^{-5} %	The role of this microelement is not fully understood yet.	Is used in treating leukemia and various cancers, viral and bacterial diseases. It is being tested in treating early stages of AIDS.
V	4.2/70 kg of a body mass or 6.0×10^{-3}%	The role of this microelement is not fully understood yet.	Vanadium is used in cancer therapy as well as in treating viral, bacterial and fungal diseases.

GLOSSARY

Absorption is a physiochemical process in which atoms, molecules, or ions enter some bulk phase — gas, liquid, or solid material.

Acceptor is an atom providing a vacant orbital.

Acid polyelectrolytes contain ionosable groups that are proton donors.

Activated carbon is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder.

Adsorbate is the material concentrated at the surface of that phase.

Adsorbent is the adsorbing phase.

Adsorption is the attachment of particles of adsorbates to the surface of adsorbents.

Adsorption layer is built up of potential determining ions and counter ions involved into a colloidal particle.

Aggregation methods are condensation of atoms, ions and molecules into colloidal dispersed particles.

Aluminosilicates are the class of minerals containing aluminum and silicon oxides.

Amphiprotic polyelectrolytes contain both acid and base ionosable groups.

An aggregate is a group of particles (which may be atoms or molecules) held together in any way

Angular momentum (orbital) quantum number (ℓ) takes the integral values from 0 to (n-1). It determines the shape of the orbital and a number of subshells within a shell.

Atom is a micro system composed of a positively charged nucleus and negatively charged electron shell.

Atomic number (N) is a fundamental characteristic of an atom. It is equal to the number of protons in atomic nucleus and its electric charge.

Atomic orbital *(AO)* is the area of space around the nucleus characterized by high probability to find electron in it (no less than 90%).

Atomic Orbital Radius is a theoretically calculated distance from the nucleus to the maximum of electron density in the outer orbital (R, nm).

Base polyelectrolytes contain ionosable groups that are proton acceptors.

Bond Energy (E, kJ/mol) is the amount of energy required to break a particular bond in a mole of molecules in a gaseous state.

Bond order (n) equals to the number of electron pairs shared by two atoms.

Brownian motion is the random chaotic movement of particles in a colloidal dispersion caused by collision between the dispersed particles and the molecules of a dispersion medium.

Capillary electrophoresis (CE) is an analytical technique in which molecules with different electrophoretic mobilities are separated by applying an external electric field. CE has applications to drug discovery and screening, clinical analysis, and pathogen detection

Chemical aggregation is based on chemical reactions taking place in aqueous solutions which run with the formation of solid insoluble substances.

Chemical bond is the result of interaction between atoms which gives stable polyatomic systems.

Chemical element is a type of atoms with the same atomic number.

Chemisorption. In chemical adsorption the molecules (or atoms) stick to the surface by forming a chemical (usually covalent) bond.

Chromatography is the process of separating the components of mixtures that are distributed between a *stationary phase* and a flowing *mobile phase* according to the rate at which they are transported through the stationary phase.

Coagulation is the irreversible aggregation of dispersed particles into large particles followed by rapid precipitation.

Colloidal chemistry is a chemistry of dispersed systems.

Colloidal particle is a compartment of a micelle, composed of an aggregate and an adsorption layer

Colloidally stable means that the particles do not aggregate at a significant rate.

Configuration is a stereo arrangement of atoms in a molecule.

Counter ions are ions which are adsorbed on the surface of nuclei; they are involved in adsorption and diffusion layers separately.

Covalence number of an atom can be predicted as a number of unpaired electrons in its ground and energetically excited states.

Covalent Bond is a bond formed by the sharing of one, two or three pairs of electrons by two atoms.

Critical coagulation concentration (γ) is a minimal amount of an electrolyte which starts coagulation in 1 L of a sol.

Degenerate orbitals are the orbitals that have the same energy.

Dialysis is a phenomenon like osmosis except that in dialysis not only water molecules but also ordinary-sized ions and molecules can move through the membrane.

Diamagnetic substances contain only paired electrons and are slightly repelled by a magnet.

Diffusion is a motion of particles down a concentration gradient.

Diffusion layer involves counter ions that are outside a colloidal particle. At the result of ions adsorption colloidal particles acquire a definite electric charge.

Dipole moment (μ) is the measure of the overall polarity of a covalent bond**.** It is calculated as **$\mu = \ell \times q$,** where ℓ is a distance between negative and positive poles in a molecule, and q is an effective charge of atoms in a molecule.

Dispersed system is a micro heterogeneous system composed of very fine particles of dispersed phase distributed in a dispersion medium.

Donor is an atom donating an electron pair for the formation of a bond.

Donor-acceptor mechanism is operating when one atom donates a lone electron pair to the vacant orbital of another atom.

Double electric layer (DEL) is responsible for generation of an electric potential at the boundary between adsorption and diffusion layers.

Electrokinetic properties of sols appear when electric current is passed through a colloidal solution. The most important among them are: electrophoresis and electroosmosis.

Electrokinetic potential (ξ-potential) is the electric potential generated at the boundary between adsorption and diffusion layers in a micelle. It defines stability of a colloidal particle and a distance between cells in vivo.

Electron Affinity (F, kJ/mol) is the energy change when electron is accepted by an atom: $E + \bar{e} \rightarrow X^-$.

Electron configuration is description of all electrons in an atom, where each atomic electron can be described by a set of four quantum numbers.

Electron spin quantum number (m_s) characterizes two possible spinning motions of an electron, one clockwise and the other counter clockwise. It takes the value of + ½ and - ½.

Electronegativity is the ability of an atom to attract electrons toward itself in a chemical bond.

Electroosmosis is an electrical transfer of dispersion medium across semi permeable membrane. Its application in medicine is limited.

Electrophoresis is the motion of electrically charged dispersed particles under the influence of an electric field. **Or electrophoresis** is the migration of charged molecules in a solution in response to an electric field.

End-on overlap of orbitals directed towards each other.

Enterosorption is a method to bind and remove toxins in intestinal tract of patients.

Four quantum numbers are four fundamental characteristics of the energy state of orbital.

«Gold number» is a minimal mass of a surfactant or polymer which is required to protect 10 mℓ of gold dispersion from coagulation by 1 mℓ of 10% NaCl solution.

Ground-state configuration. There are an infinity number of acceptable sets of quantum numbers, but only one set describes an atom in its most form.

Heisenberg uncertainty principle the exact momentum and position of the electron cannot be simultaneously determined.

Hemo-, lymph- and plasma-sorption are used for blood and other biological fluids purification from toxins by passing of fluids through a column filled with activated carbon or some other sorbents

Hemoglobin electrophoresis is a test that measures the different types of hemoglobin in the blood.

Hund’s rule: the most stable arrangement of electrons in subshells is the one with the greatest number of parallel spins**.**

Hybridization is the process of mixing the atomic orbitals in an atom to generate a set of new atomic orbitals with different spatial distributions. Hybridization requires an input of energy; however, the system more than recovers this energy during bond formation.

Hybridized orbitals are assumed to be mixtures of these atomic orbitals, superimposed on each other in various proportions.

Hydrogen bond is a special type of dipole-dipole interaction between the hydrogen atom bonded to an electronegative atom (for example, O-H or N-H) and another electronegative atom.

Intramolecular hydrogen bonds are responsible for stabilizing of biopolymers configurations (proteins, nucleic acids and polysaccharides).

Ion exchange adsorption process loosely helds ions at fixed-charged sites on solids are exchanged with ions that are dissolved in solutions.

Ionic bond is a type of chemical bond that involves a metal and a non-metal ion (or polyatomic ions such as ammonium) through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions.

Ionites or **ionic exchangers** are solid adsorbents able to take part in ionic exchange adsorption.

Ionization Energy (I, kJ/mol) is the minimum amount of energy required to remove an electron from a gaseous atom in its ground state: Energy + E → $E^+ + \bar{e}$

Isoelectric point (pI) is the pH of a solution at which the net charge on a macromolecule is zero**.**

Isotopes (Greek *isos* is «equal», *tópos* is «site, place») are any of the different types of atoms of the same chemical element, each having a different atomic mass (mass number).

Liposome is a super molecular structure composed of phospholipids bilayer and an interior solution

Lyotropic series are the groups of ions that carry identical electrical charge but exhibit different adsorptivity.

Macromolecule (polymer) is a chemical species distinguished by a high molar mass ($10^4 – 10^{10}$ g/mol) and by a length is approximately 10^{-6} m.

Magnetic quantum number (m_ℓ) describes orientation of the orbital in space and a number of orbitals within a subshell.

Mass number (A) is equal to the number of protons (the charge of the nucleus or its atomic number) Z plus the number of neutrons N: $A = Z + N$.

Medical physics is a branch of physics applied to medicine and biology and is an expanding field as a separate discipline.

Micelle is a solid dispersed particle surrounded by a double electric layer composed of electrolyte-stabilizer ions.

Molecular adsorption is the adsorption of non electrolytes or weak electrolytes from gaseous and liquid phases.

Molecular orbital energy-level diagrams are applied to describe the structure of molecules and molecular ions.

Monodispersed compounds are polymeric systems whose molecules have equal molar masses.

Neutron-proton ratio (N/Z). It was proved that for stable light elements $N/Z \approx 1$, and for unstable ones $N/Z > 1$. For stable heavy elements $N/Z < 1.5$, and for unstable ones $N/Z > 1.5$.

Panet-Phayans Rules. RULE 1. Solid surfaces adsorb those ions that are included into their composition. These ions are defined **as potential determining ions** or **PDI**. **RULE 2.** A charged surface adsorbs only oppositely charged ions (counter ions).

Paramagnetic substances contain one or more unpaired electrons and are attracted by a magnet

Partial negative charge (-δ) is a charge of higher electronegative atom in the bond of dipole molecule.

Partially positive charge (+δ) is a charge of less electronegative atom in the bond of dipole molecule.

Pauli's Exclusion Principle: no two electrons in an atom can have the same four quantum numbers.

Peptization method is a preparing of sols by addition of electrolytes to a freshly precipitated solid substance that is insoluble in water.

Physical adsorption is result of van der Waals interactions between adsorbents and adsorbates.

Physical aggregation involves cooling and pressure elevating of gases and vapors (formation of fogs and clouds in nature), and substitution of solvents in solutions.

Polydispersed compounds are polymeric systems whose molecules have different molar masses.

Polyelectrolytes are polymers which contain ionosable groups.

p-Orbitals are nonspherical; the orbitals place most of the electron density in two «lobes» along one of the X-, Y-, or Z-axes on either side of the nucleus. These three p orbitals are identical in size, shape and energy; they differ from one another only in orientation.

Potential determining ions (PDI) are ions which are adsorbed at the surface of aggregates.

Principal quantum number (n) can have integral values 1, 2, 3, 4 and so forth. It determines the total energy of an orbital and also relates to the average distance of the electron from the nucleus in a particular orbital.

π- Bond is result of a side-by-side overlap of atomic orbitals.

Schulze-Hardy Rule: hydrophobic colloids are coagulated most efficiently by ions of opposite charge and high charge number.

Sedimentation is the settling of suspended particles under the action of gravity.

Side-by-side overlap of atomic orbitals is above and below the bond internuclear axis.

Sigma bonds have high electron density distributed symmetrically along the bond axis.

Silica gel is a dehydrated gel of polysilicon acids $(SiO_2)_n$.

Solid sorbents are natural or artificial substances with highly developed surface area.

s-Orbitals are spherical and increase in the size with increasing **n.**

Surface phenomena are those processes, which run spontaneously at the interface surfaces.

Surface tension is the amount of free surface energy per area unit.

Surfactants or surface-active agents are substances that reduce surface tension of water.

Swelling is a spontaneous irreversible diffusion of solvent molecules into a polymer phase. Non-limited swelling results in formation of true solutions. Limited swelling results in gels formation.

Traube's Rule (1884): the surface tension of the organic compounds belonging to the homological series of $R(CH_2)n$ X shows certain regularity. For each additional CH_2 group the surface activity is increased by factor 3–3.5.

Ultrafiltration is the application of pressure or suction to force the solvent and small particles across a membrane while the larger particles are retained

Valence electrons are the outer electrons of an atom which are involved in chemical bonding.

VB theory assumes that the electrons in a molecule occupy atomic orbitals of the individual atoms.

Wave-particle duality is a phenomena shows what electrons can act as particles and also as waves.

Zeolites are natural or synthetic crystalline aluminosilicates which have a repeating pore network and release water at high temperature.

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