

МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ
БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ
КАФЕДРА ОБЩЕЙ ХИМИИ

**ТЕОРЕТИЧЕСКИЕ ОСНОВЫ
СТРОЕНИЯ ВЕЩЕСТВА**

**Basic concepts about
the STRUCTURE of matter**

Учебно-методическое пособие



Минск БГМУ 2009

УДК 547.9 (811.111) (075.8)
ББК 24.23 (81.2 Англ – 923)
Т 33

Рекомендовано Научно-методическим советом университета в качестве
учебно-методического пособия 24.06.2009 г., протокол № 10

А в т о р ы: ст. преп. С. Р. Казюлевич; доц. С. В. Ткачѐв; доц. Т. В. Латушко;
проф. Е. В. Барковский

Перевод с русского языка: С. В. Ткачѐва (БГМУ); С. Ч. Папук (БГУ)

Р е ц е н з е н т ы: доц. О. Н. Ринейская; доц. А. В. Колб

Теоретические основы строения вещества = Basic concepts about the structure
Т 33 of matter : учеб.-метод. пособие / С. Р. Казюлевич [и др.] ; пер. с рус. яз.
С. В. Ткачѐва, С. Ч. Папук. – Минск : БГМУ, 2009. – 48 с.

ISBN 978–985–462–997–1.

Издание содержит материал по современным представлениям о строении вещества: строение электронной оболочки атомов и принципы ее заполнения электронами, основные концепции химической связи, строение комплексных соединений, их свойства и значение в медицине, теория гетерогенного равновесия, условия образования и растворения осадков, гетерогенное равновесие в биологических системах.

Предназначено для студентов 1-го курса медицинского факультета с обучением на английском языке.

УДК 547.9 (811.111) (075.8)
ББК 24.23 (81.2 Англ – 923)

Учебное издание

Казюлевич Светлана Ричардовна
Ткачѐв Сергей Викторович
Латушко Татьяна Викторовна
Барковский Евгений Викторович

ТЕОРЕТИЧЕСКИЕ ОСНОВЫ СТРОЕНИЯ ВЕЩЕСТВА BASIC CONCEPTS ABOUT THE STRUCTURE OF MATTER

Учебно-методическое пособие на английском языке

Ответственный за выпуск Е. В. Барковский
В авторской редакции
Компьютерный набор Е. П. Ковгарени
Компьютерная верстка Н. М. Федорцовой

Подписано в печать 25.06.09. Формат 60×84/16. Бумага писчая «КюмЛюкс».

Печать офсетная. Гарнитура «Times».

Усл. печ. л. 2,79. Уч.-изд. л. 2,48. Тираж 45 экз. Заказ 533.

Издатель и полиграфическое исполнение:
учреждение образования «Белорусский государственный медицинский университет».

ЛИ № 02330/0494330 от 16.03.2009.

ЛП № 02330/0150484 от 25.02.2009.

Ул. Ленинградская, 6, 220006, Минск.

ISBN 978–985–462–997–1

© Оформление. Белорусский государственный
медицинский университет, 2009

PREFACE

This chemistry guide for the first year students is based on the lectures which are being delivered in the Byelorussian state medical university. It aims at providing a sound base for understanding the basic principles of general chemistry.

As you know chemistry is based on the idea that matter is composed of particles such as electrons, protons and neutrons. They are organized into atoms, and these atoms further combine to form molecules. These aspects have been explained in chapter one.

Chapter two includes the modern theories of chemical bonding and enables the students to understand the geometry of simple molecules.

The ions of some elements can attach other ions or neutral molecules and form more elaborate complex ions when the latter combine with ions of the opposite sign, various complex compounds are obtained. Chapter three describes the formation and properties these complex compounds.

General chemistry is closely connected with biology and medicine through biochemistry. In conjunction with pharmacology and medicine biochemistry will find ever more powerful means for fighting diseases. Chapter four describes the theory of heterogeneous equilibria and explains their biochemical influence on the formation on bone tissue in a human body.

It is hoped that the guide will serve the needs of the students with respect to examination. We are conscious of the possible printing errors in this guide. We would welcome if these errors are brought to our notice.

CHAPTER I

The electron shell of the atom. electron configurations of elements. The periodic table. atomic properties and periodic trends

The atom is a complicated microsystem consisting of the moving elementary particles. It consists of a positively charged nucleus and negatively charged electrons. The main characteristics of the electron, proton, and neutron are given in table 1.

Table 1

The Main Characteristics of Elementary Particles

Particle	Symbol	Rest mass, kg	Charge, C
Proton	p	1.673×10^{-27}	$+1.602 \times 10^{-19}$
Neutron	n	1.675×10^{-27}	0
Electron	e	9.1×10^{-31}	-1.602×10^{-19}

The properties of the nucleus depend mainly on its composition, i. e. on the number of protons and neutrons. The number of protons in the nucleus identifies the charge of the nucleus and its belonging to a given chemical element. Another important characteristic of the nucleus is the mass number (sign A) which is equal to the total number of protons (sign Z) and neutrons (sign N) in it as:

$$A = Z + N.$$

Atoms with the same number of protons and with the different mass number are called isotopes. For example, chemical element hydrogen has three isotopes ^1H , ^2H , ^3H (where 1, 2 and 3 are mass numbers).

1. THE ELECTRON SHELL OF THE ATOM

1.1. Energy levels.

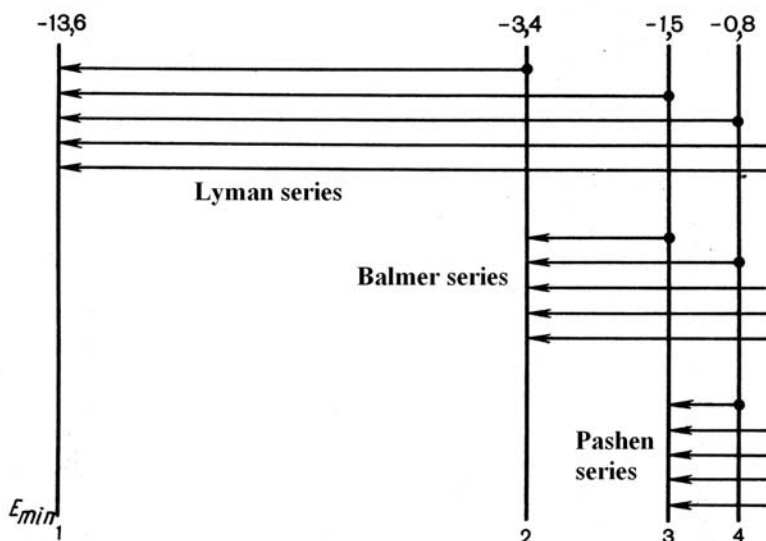


Fig. 1. Diagram of the energy levels and quantum transitions of the electron of a hydrogen atom

Niels Bohr in 1913 made the revolutionary suggestion that the total energy (kinetic plus potential) of an electron in an atom is quantized, i. e., restricted to having only certain values. This means that in an atom an electron cannot have any energy but only certain specific values. The only way an electron can change its energy is to shift from one discrete energy level to another.

If the electron is at a lower energy level, it can radiate energy, but only a definite amount. This amount of energy is equal to the difference between one energy level and another (figure 1). The Bohr's theory established the basis for quantum mechanics. It studies motion laws that govern the behavior of small particles.

1.2. The wave nature of microparticles motion. It was known that all electromagnetic radiation could be described by the physics of waves, where the product of wavelength (λ) and frequency (ν) are equal to the velocity of light ($c = 2.998 \times 10^8$ m/s):

$$\lambda\nu = c$$

In 1924 Louis de Broglie proposed that an electron and other particles of comparable mass could also be described by the physics of waves. De Broglie suggested the extending corpuscular-wave concept to all microparticles, in which the motion of any microparticle is regarded as a wave process. Mathematically this is expressed by the de Broglie equation, according to which a particle of mass (m) moving at a velocity (v) has a certain wavelength (λ): $\lambda = h/mv$, where h is the Planck's constant.

De Broglie's hypothesis was proved experimentally by the discovery of diffraction and interference effects in a stream of electron. According to the de Broglie equation the motion of an electron with the mass equal to 9.1×10^{-31} kg and the velocity equal to 10^8 m/s is associated with a wavelength equal to 10^{-10} metres, i. e. the wavelength approximately equals to the atom's size. When a beam of electrons is scattered by a crystal, diffraction is observed. The crystal acts as a diffraction lattice.

1.3. The uncertainty principle. In 1927 Werner Heisenberg set for the first time the uncertainty principle according to which it is impossible to accurately determine both the position (or coordinates) and the velocity of motion of a microparticle simultaneously. The mathematical expression of the uncertainty principle is: $\Delta x \cdot \Delta v > h/2\pi m$ where Δx , Δv are uncertainties of the position and velocity of a particle respectively.

It follows from equation that the higher the accuracy of a particle the coordinate the determination, the less certain the value of its velocity is. Thus the state of an electron in an atom cannot be represented as the motion of a material particle along the orbit. Quantum mechanics uses the idea of a statistical probability of finding the electron at a definite point in space around the nucleus. The position of the electron is not know with certainty, however; only the probability of the electron being in a given region of space can be calculated.

1.4. The electron cloud. Quantum mechanics is a new branch of physics. It describes the motion and interaction of microparticles. The model of an electron in an atom accepted in quantum mechanics is the idea of an electron cloud. Let us assume that we have photographed the position of an electron at some

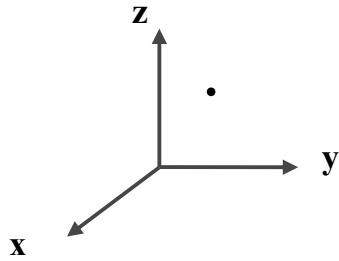


Fig. 2. The position of an electron

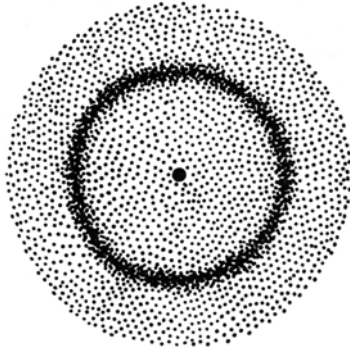


Fig. 3. A possible form of the electron cloud in an atom

The space around the nucleus in which the probability of finding the electron is the highest is called the orbital. The configuration and size of the electron cloud is usually regarded as the shape and size of the orbital.

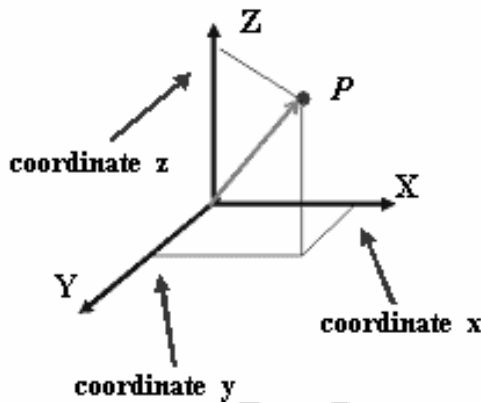


Fig. 4. The Cartesian coordinate system. The position of a point P in space can be specified by giving the x, y and z coordinates

moment of time in the three-dimensional space around the nucleus. The position of an electron is shown on the photographs as a dot (figure 2). If we repeat the experience thousands of times, the new photographs taken at short intervals, will discover the electron in new positions. When all the photographs are superimposed on one another, we will get a picture resembling a cloud. A possible form of the electron cloud in an atom is shown in figure 3.

The cloud will be the densest where the number of dots is the greatest, i. e. where probability of finding the electron in the cloud is the highest.

The stronger the bond between the nucleus and the electron the smaller the electron cloud will be and the denser the distribution of the charge. The space around the nucleus in which the probability of finding the electron is the highest is called the orbital.

1.5. The quantum numbers.

In a three-dimensional world, three parameters are required to describe the location of an object in space (figure 4). The position of a point P in space can be specified by giving the x, y, and z coordinates.

For the atomic electron, this requirement leads to the existence of three quantum numbers: n , ℓ and m_ℓ , which define an orbital by giving the electron shell, the subshell, and the orbital within that subshell.

In case of the hydrogen atom, the first of these three quantum numbers alone is sufficient to describe the energy

of the electron, but all three are needed to define the probability of finding that electron in a given region of space.

The principal quantum number n can have any integer value from 1 to infinity: $n = 1, 2, 3, \dots$. It is the most important quantum number because its value determines the total energy of the electron. The value of n also gives

a measure of the most probable distance of the electron from the nucleus: the greater the value of n , the more probable it is that the electron is found further from the nucleus.

An earlier notation used letters for the major electron shells: K, L, M, N, and so on, corresponding to $n = 1, 2, 3, 4$ and so on. That is, n is a measure of the orbital radial size or diameter.

In atoms having more than one electron, two or more electrons may have the same n value. These electrons are then said to be in the same electron shell, the shells being numbered according to their major quantum number.

The angular momentum quantum number ℓ is related to the shape of electron orbitals, and the number of values of ℓ for a given value of n states how many different orbital types or electron subshells there are in a particular electron shell: ℓ , the angular momentum quantum number = $0, 1, 2, \dots (n - 1)$.

The integer values that ℓ may have are limited by the value of n : ℓ may be an integer from 0 up to and including $n - 1$. In other words, if n is 1, then there is only one ℓ value possible; ℓ can only be 0, and there can only be one type of the orbital or subshell in the $n = 1$ electron shell. In contrast, when $n = 4$, ℓ can have four values of 0, 1, 2, and 3. Because there are four values of ℓ , there are four orbital types or four subshells within the fourth major quantum shell.

The values of the ℓ quantum number are usually coded by a letter according to the scheme below.

Value of ℓ	Corresponding orbital label
0	s
1	p
2	d
3	f

Thus, for example, a subshell with a label of $\ell = 1$ is called a «p subshell» and an orbital found in that subshell is called a «p orbital».

Electron orbitals are labeled by first giving the value of n and then the value of ℓ in the form of its letter code. For $n = 1$ and $\ell = 0$, the label is 1s.

For a given n , there will be n values of ℓ and n orbital types; this means there is a total of n^2 orbitals in the n th shell.

Magnetic quantum number. The first quantum number (n) locates the electron in a particular electron shell, and the second (ℓ) places it in a particular subshell of orbitals within the shell.

The third quantum number (m_ℓ) then specifies in which orbital within the subshell the electron is located; m_ℓ is related to the spatial orientation of an orbital in a given subshell.

The number of m_ℓ values = the number of orbitals in a subshell. The integer values that m_ℓ may have are limited by ℓ ; m_ℓ values can range from $+\ell$ to $-\ell$ with 0 included: $m_\ell = 0, \pm 1, \pm 2, \pm 3, \dots \pm m_\ell$.

For example, when $\ell = 2$, m_ℓ has the five values $+2, +1, 0, -1, -2$. The number of values of m_ℓ for a given ℓ states how many orbitals of a given type there are in that subshell (table 2).

Table 2

Summary of the quantum numbers, their interrelationships

Principal quantum number	Angular momentum	Magnetic quantum number	Number and type of orbitals in the subshell
Symbol = n Values = 1, 2, 3... (Orbital size, Energy)	Symbol = ℓ Values = 0... (n-1) (Orbital Shape)	Symbol = m_ℓ Values = -1...0...+1 (Orbital Orientation)	Number = number of values of $m_\ell = 2\ell + 1$ (Orbitals in a Shell = n^2)
1	0	0	1 1s orbital (1 orbital in the $n = 1$ shell)
2	0 1	0 +1, 0, -1	1 2s orbital 3 2p orbital (4 orbitals of 2 types in the $n = 2$ shell)
3	0 1 2	0 +1, 0, -1 +2, +1, 0, -1, -2	1 3s orbital 3 3p orbital 5 3d orbital (9 orbitals of 3 types in the $n = 3$ shell)
4	0 1 2 3	0 +1, 0, -1 +2, +1, 0, -1, -2 +3, +2, +1, 0, -1, -2, -3	1 4s orbital 3 4p orbital 5 4d orbital 7 4f orbital (16 orbitals of 4 types in the $n = 4$ shell)

Electron spin. Three quantum numbers (n , ℓ and m_ℓ) allow us to define the orbital for an electron. To describe completely an electron in an atom with many electrons, however, we still need one more quantum number, the electron spin quantum number, m_s .

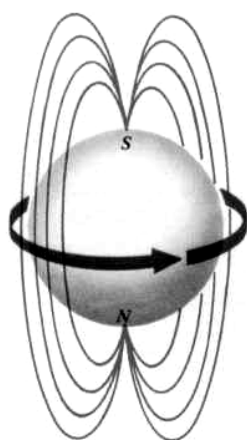


Fig. 5. Electron spin

In approximately 1920, theoretical chemists realized that, since electrons interact with a magnetic field, there must be one more concept to explain the behavior of electrons in atoms.

It was soon verified experimentally that the electron behaves as though it has a spin. This spin is much like that of the earth spinning on its axis and, since the electron is electrically charged, the spinning charge generates a magnetic field with north and south magnetic poles (figure 5); that is, the electron acts like a tiny bar magnet.

The properties of magnets are related to the number of unpaired electrons in the atoms of which the magnet is composed. Thus, as expected, hydrogen atoms are paramagnetic to the extent of one unpaired electron. Helium atoms, which have two electrons, are not paramagnetic, however. The explanation for this experimental observation rests on two hypotheses: (1) the two electrons are assigned to the same orbital and (2) electron spin is quantized. The quantization of electron spin means that there are only two possible orientations of an electron in a magnetic field, one associated with a spin quantum number, m_s , of $+1/2$ and the other with an m_s value of $-1/2$. To account for the lack of paramagnetism of helium, we must assume the two electrons assigned to the same orbital have opposite spin directions; we say they are paired. The implications of this observation are enormous and open the way to explain the electron configurations of atoms with more than one electron.

1.6. The shapes of atomic orbitals. When an electron has a value of $\ell = 0$, we say the electron occupies an s orbital.

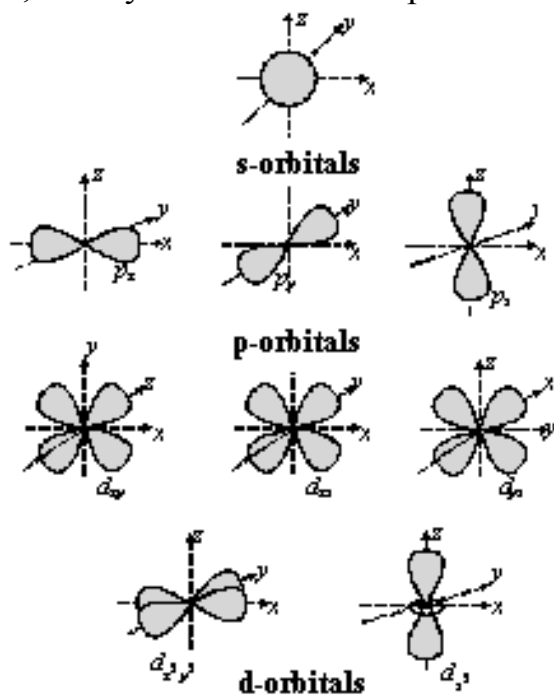


Fig. 6. The shapes of atomic orbitals

When $\ell = 2$, then m_ℓ can only be $+2, +1, 0, -1$ and -2 . There are five types of $\ell = 2$ or d orbitals.

2. ELECTRON CONFIGURATIONS OF ELEMENTS

2.1. The Pauli principle. To make the quantum theory consistent with experiment, Wolfgang Pauli stated in 1925 the Pauli exclusion principle: no two electrons in an atom can have the same set of four quantum numbers (n , ℓ , m_ℓ and m_s). This principle leads to yet another important conclusion, that no atomic orbital can be assigned to (or «contain») more than two electrons. If we

All s orbitals are spherical in shape, but the $2s$ cloud is larger than the $1s$ cloud (figure 6.): the point of maximum probability for the $2s$ electron is found slightly farther from the nucleus than that of the $1s$ electron.

Atomic orbitals for which $\ell = 1$ are called p orbitals.

According to table 2, when $\ell = 1$, then m_ℓ can only be $+1, 0$, and -1 . That is, there are three types of $\ell = 1$ or p orbitals. Since there are three mutually perpendicular directions in space (x , y , and z), the p orbitals are commonly visualized as lying along these directions, and they are labeled according to the axis along which they lie (p_x , p_y and p_z).

consider the 1s orbital of the H atom, this orbital is defined by the set of quantum numbers $n = 1$, $\ell = 0$ and $m_\ell = 0$. No other set of numbers can be used. If an electron has this orbital, the electron spin direction must also be specified.

The orbital is shown as a «box» and the electron spin in one direction is depicted by an arrow:

Electron in 1s orbital	Quantum Number Set
$\boxed{\uparrow}$	$n = 1, \ell = 0, m_\ell = 0, m_s = +1/2$

If there is only one electron with a given orbital, you can picture the electron as an arrow pointing either up or down.

Thus, an equally valid combination of quantum numbers and a «box» diagram would be:

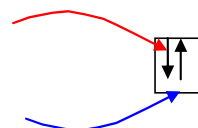
Electron in 1s orbital	Quantum Number Set
$\boxed{\downarrow}$	$n = 1, \ell = 0, m_\ell = 0, m_s = -1/2$

The pictures above are appropriate for the H atom in its ground state: one electron in the 1s orbital.

For the helium atom, the element with two electrons, both electrons are assigned to the 1s orbital. From the Pauli principle, you know that each electron must have a different set of quantum numbers, so the orbital box picture now is

Two electrons in the 1s orbital of He atom:

this electron has $n = 1, \ell = 0, m_\ell = 0, m_s = -1/2$
 this electron has $n = 1, \ell = 0, m_\ell = 0, m_s = +1/2$



2.2. The Order of orbital energies and assignments. Generally, electrons are assigned to orbitals of successively higher energies because this will make the total energy of all the electrons as low as possible. The order of orbital energies is given in figure 7.

Here you see that orbital energies of many-electron atoms depend on both n and ℓ . The orbitals with $n = 3$, for example, do not all have the same energy; rather, they are in the order $3s < 3p < 3d$. The orbital energy order in figure 7, and the determination of the actual electron configurations of the elements, lead to two general rules for the order of assignment of electrons to orbitals.

1. Orbital assignments follow a sequence of increasing $n + \ell$.
2. For two orbitals of the same $n + \ell$, electrons are assigned first to orbitals of lower n .

These rules mean electrons are usually assigned in order of increasing orbital energy. However, there are exceptions. For example, electrons are assigned to a 4s orbital ($n + \ell = 4$) before being assigned to 3d orbitals ($n + \ell = 5$). This order of assignment is observed in spite of the fact that the energies of these orbitals are in the order $3d < 4s$ (figure 7).

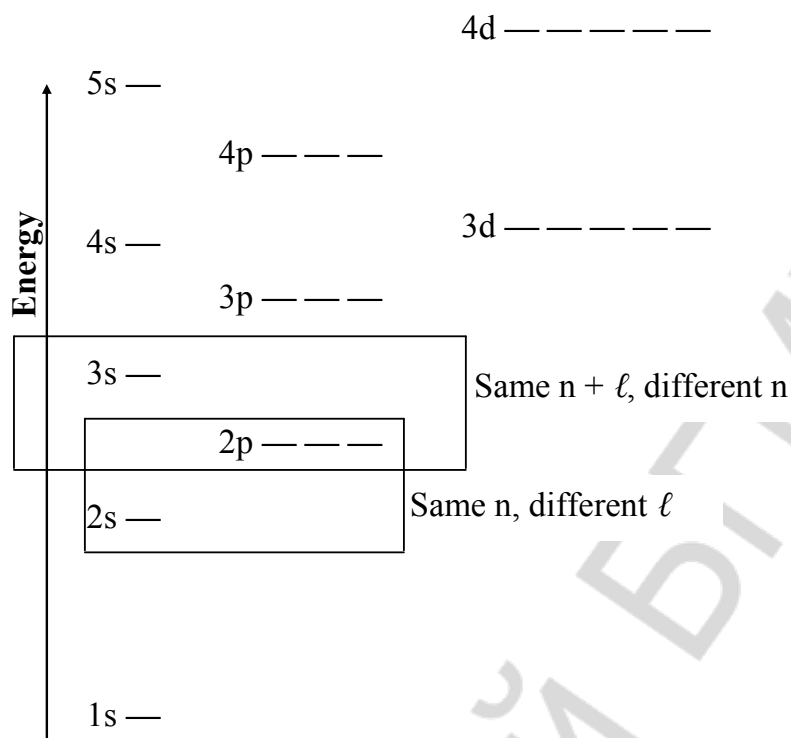


Fig. 7. The order of orbital energies

2.3. Electron configurations of the main group elements. Configurations of the first ten elements are illustrated in table 3. The first two electrons must be assigned to the 1s orbital, so the third electron must use the $n = 2$ shell. According to the energy level diagram in figure 7, that electron must be assigned to the 2s orbital. The spectroscopic notation: $1s^2 2s^1$ is read as «one es two, two es one».

The position of Li atom in the periodic table tells you its configuration immediately. All the elements of Group 1A (and IB) have one electron assigned to an s orbital of the nth shell, where n is the number of the period in which the element is found.

For example, potassium is the first element in the $n = 4$ row, so potassium has the electron configuration of the element preceding it in the table (Ar) plus a final electron assigned to the 4s orbital.

Copper, in Group IB, will also have one electron assigned to the 4s orbital, plus 28 other electrons assigned to other orbitals.

The configuration of Be $1s^2 2s^2$. All elements of Group 2A have electron configurations [electrons of preceding rare gas + ns^2], where n is the period in which the element is found in the periodic table.

At boron (Group 3A) you first encounter an element in the block of elements on the right side of the periodic table. Since the 1s and 2s orbitals are filled in a boron atom, the fifth electron must be assigned to a 2p orbital, the configuration of B atom $1s^2 2s^2 2p^1$. In fact, all the elements from Group 3A through Group 8A are characterized by electrons assigned to p orbitals, so these

elements are sometimes called the p block elements. All have the general configuration of ns^2np^x where $x = \text{group number} - 2$.

Table 3

Electron configurations of the elements with $Z = 1$ to 10

	ℓ m_ℓ	$1s$ 0 0	$2s$ 0 0	$2p$ 1 $+1 \quad 0 \quad -1$
H $1s^1$		\uparrow	\square	$\square \quad \square \quad \square$
He $1s^2$		$\uparrow\downarrow$	\square	$\square \quad \square \quad \square$
Li $1s^2 2s^1$		$\uparrow\downarrow$	\uparrow	$\square \quad \square \quad \square$
Be $1s^2 2s^2$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\square \quad \square \quad \square$
B $1s^2 2s^2 2p^1$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \quad \square \quad \square$
C $1s^2 2s^2 2p^2$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \quad \uparrow \quad \square$
N $1s^2 2s^2 2p^3$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow \quad \uparrow \quad \uparrow$
O $1s^2 2s^2 2p^4$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \quad \uparrow \quad \uparrow$
F $1s^2 2s^2 2p^5$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow$
Ne $1s^2 2s^2 2p^6$		$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow$

Carbon (Group 4A) is the second element in the p block, so there is a second electron assigned to the 2p orbitals: the configuration of C $1s^2 2s^2 2p^2$.

In general, when electrons are assigned to p, d or f orbitals, each electron is assigned a different orbital of the subshell, each electron having the same spin as the previous one; this proceeds until the subshell is half full, after which pairs of electrons must be assigned a common orbital.

This procedure follows the **Hund's rule**, which states that the most stable arrangement of electrons is that with the maximum number of unpaired electrons, all with the same spin direction. Electrons are negatively charged particles, so assignment to different orbitals minimizes electron-electron repulsions, making the total energy of the set of electrons as low as possible. Giving them the same spin also lessens their repulsions.

2.4. Electron configurations of the transition elements. The 3s and 3p subshells are filled at argon, and the periodic table indicates that the next element is potassium, the first element of the fourth period. This means, though,

that potassium must have the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ ($[\text{Ar}]4s^1$), a configuration given by the $(n + \ell)$ rule.

After electrons have been assigned to the 4s orbital, the 3d orbitals are those next utilized. Accordingly, scandium must have the configuration $[\text{Ar}]3d^1 4s^2$ and titanium follows with $[\text{Ar}]3d^2 4s^2$ and vanadium with $[\text{Ar}]3d^3 4s^2$. Notice in the orbital box diagrams in table 4 that one electron is assigned to each of the five possible d orbitals and that all have the same spin direction.

On arriving at chromium, we come to what some might call an anomaly in the order of orbital assignment. For complex reasons, among them the minimization of electron-electron repulsions, chromium has one electron assigned to each of the six available 4s and 3d orbitals.

Table 4

Orbital Box Diagrams for the Elements Ca Through Zn

		3d					4s	=
		+2	+1	0	-1	-2	0	
Ca	$[\text{Ar}] 4s^2$						$\uparrow\downarrow$	
Sc	$[\text{Ar}] 3d^1 4s^2$	\uparrow					$\uparrow\downarrow$	
Ti	$[\text{Ar}] 3d^2 4s^2$	\uparrow	\uparrow				$\uparrow\downarrow$	
V	$[\text{Ar}] 3d^3 4s^2$	\uparrow	\uparrow	\uparrow			$\uparrow\downarrow$	
Cr*	$[\text{Ar}] 3d^5 4s^1$	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow	
Mn	$[\text{Ar}] 3d^5 4s^2$	\uparrow	\uparrow	\uparrow	\uparrow	\uparrow	$\uparrow\downarrow$	
Fe	$[\text{Ar}] 3d^6 4s^2$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	\uparrow	$\uparrow\downarrow$	
Co	$[\text{Ar}] 3d^7 4s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	$\uparrow\downarrow$	
Ni	$[\text{Ar}] 3d^8 4s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	$\uparrow\downarrow$	
Cu*	$[\text{Ar}] 3d^{10} 4s^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	
Zn	$[\text{Ar}] 3d^{10} 4s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	

3. THE PERIODIC TABLE. ATOMIC PROPERTIES AND PERIODIC TRENDS

3.1. Atomic size. For the main group elements, atomic radii increase going down a group in the periodic table and decrease going across a period (figure 8).

The reason atomic radii increase on descending a periodic group is clear. Going down Group 1A, for example, the last electron added is always assigned

to an s orbital and is in the electron shell beyond that used by the electrons of the elements in the previous period. The inner electrons shield or screen the nuclear charge from the outermost ns^1 electron, so the last electron feels an effective nuclear charge, Z , of approximately +1. Since, on descending the group, the ns^1 electron is most likely found at greater and greater distances from the nucleus, the atom size must increase.

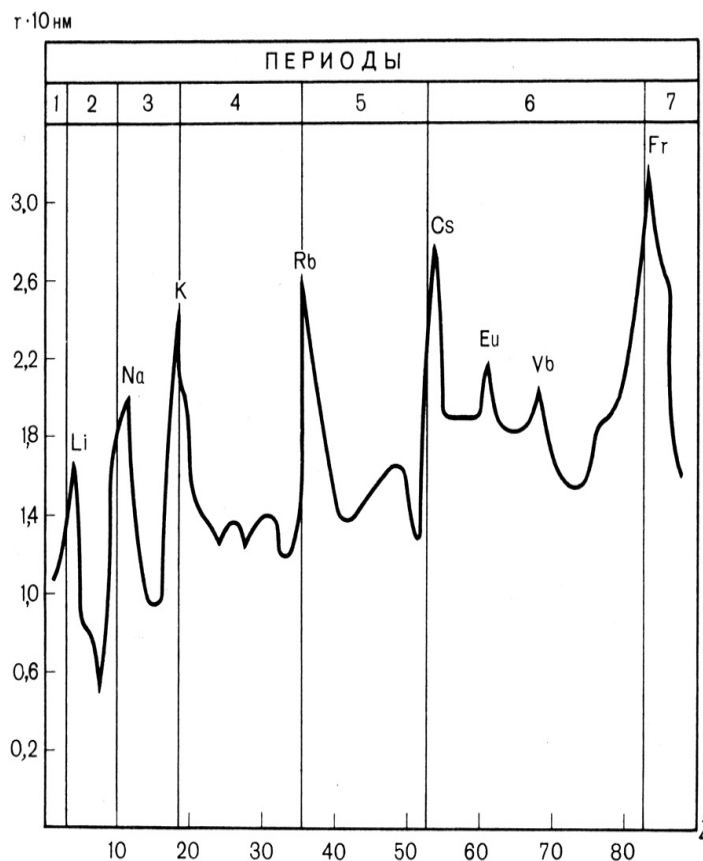


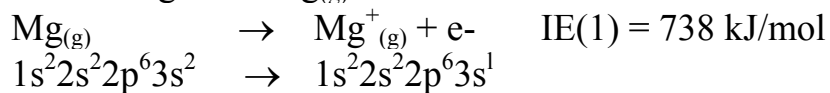
Fig. 8. Atomic radii of the elements

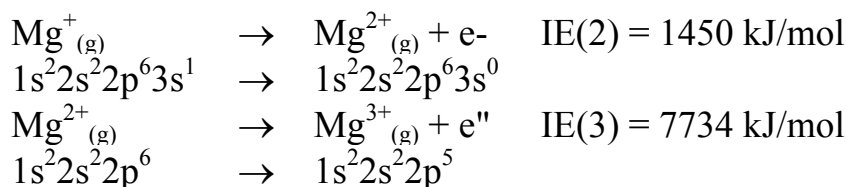
When moving across a period of main group elements, the size decreases because the effective nuclear charge increases.

3.2. Ionization energy. The ionization energy of an atom is the energy required to remove electron from an atom or ion in the gas phase: Atom in ground state_(g) + energy → Atom⁺_(g) + e⁻, ΔE = ionization energy (IE)

The process of ionization involves moving an electron from a given electron shell to a position outside the atom. Energy is always required, so the process is endothermic and the sign of the ionization energy is always positive.

Each atom can have a series of ionization energies, since more than one electron can always be removed (except for H). For example, the first three ionization energies of Mg_(g) are





For the main group or A-type elements, first ionization energies generally decrease down a periodic group and increase across a period. The ionization energy decrease going down the table occurs for the same reason that the size increases in this direction: the first-removed electron is farther and farther from the nucleus and so less and less energy is required for its removal. There is a general increase in ionization energy when moving across a period of the periodic table due to an ever increasing effective nuclear charge. The trend, however, is not smooth (figure 9), and its peaks and valleys give us further insight into atomic structure. First, in spite of the general trend, the ionization energy for boron is less than that for beryllium. The reason for this is that the 2s orbital of beryllium is lower in energy than the boron 2p orbital. Therefore, less energy is required to remove the boron 2p electron than the 2s electron of beryllium.

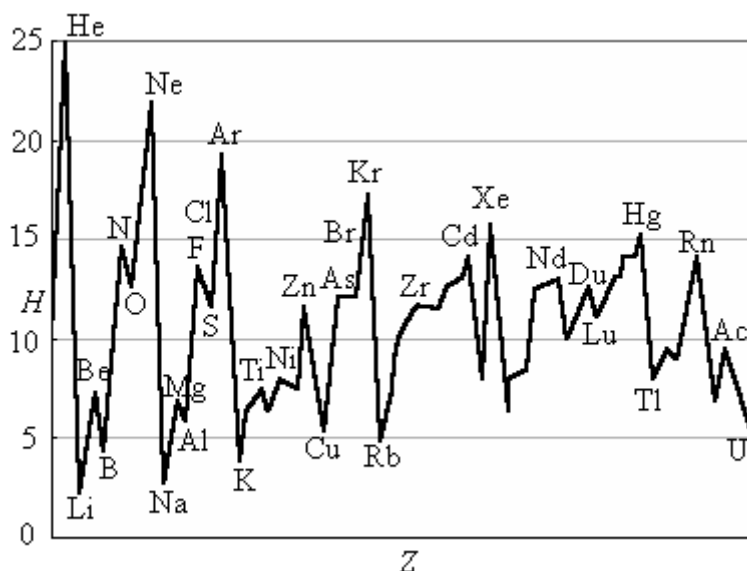
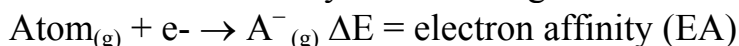


Fig. 9. First ionization energies of the elements

3.3. Electron affinity. A measure of the electron affinity of an element is the energy involved when an electron is brought from an infinite distance away up to a gaseous atom and absorbed by it to form a gaseous ion.



When a stable anion is formed, energy is released and the sign of the energy change is negative. The greater the electron affinity the more negative the value of EA. Fluorine, for example, has an electron affinity of -322 kJ/mol. The value of EA for the first ten elements is shown in table 5.

Electron Affinities for the first and the second period elements

	H	He	Li	Be	B	C	N	O	F	Ne
<i>EA</i> , эВ	0,75	-0,22	0,8	-0,19	0,30	1,27	-0,21	1,47	3,45	-0,57

$F_{(g)} + e^- \rightarrow F^-_{(g)} + 322 \text{ kJ/mol}$. The periodic trends in electron affinity are closely related to those for ionization energy and size.

There is a general increase across a period due to the general increase in Z , but there is evidence again for the competing effects of electron-electron repulsions and changes in nuclear charge. For example, just as electron-electron repulsions cause the ionization energy of oxygen to be lower than expected, the same effect means nitrogen has almost no affinity for an electron: $N_{(g)} + e^- \rightarrow N^-_{(g)}$, no energy evolved or required.

When descending a periodic group, we expect the electron affinity to decrease for the same reason that the atom size increases and ionization energy decreases.

CHAPTER II

Chemical bond

1. VALENCE ELECTRONS

The outermost electrons of an atom, are the electrons affected the most by the approaching of another atom. They are called valence electrons. The rare gas core electrons and the filled d -shell electrons of Group 3A elements are not greatly affected by reactions with other atoms, so we focus our attention on the behavior of the outer ns and np electrons (and d electrons in unfilled subshells of the transition metals). The valence electrons for a few typical elements are:

Core element	Electrons	Valence electrons	Periodic group
Na	$1s^2 2s^2 2p^6$	$3s^1$	1 A
Si	$1s^2 2s^2 2p^6$	$3s^2 3p^2$	4 A
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6$	$4s^2 3d^2$	4 B
As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	$4s^2 4p^3$	5 A

From the table above you see that the number of valence electrons of each elements is equal to the group number. The fact that every element in a given group has the same number of valence electrons accounts for the similarity of chemical properties among members of the group.

A useful device for keeping track of the valence electrons of the main group elements is the Lewis electron dot symbol, first suggested by Lewis, in 1916. In this notation, the nucleus and core electrons are represented by the atomic symbol. The valence electrons, represented by dots, are then placed around the symbol one at a time until they are used up or until all four sides are occupied; any remaining electrons are paired with the existing electrons. The Lewis symbols for the first two periods are:

1A	2A	3A	4A	5A	6A	7A	8A
ns^1	ns^2	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$
•Li	•Be•	•B•	•C•	•N•	•O•	•F•	•Ne•
•Na	•Mg•	•Al•	•Si•	•P•	•S•	•Cl•	•Ar•

The Lewis symbol emphasizes the rare gas configuration, $ns^2 np^6$, as a stable, low-energy state. In fact, the bonding behavior of the main group elements can often be considered as being the result of gaining, losing, or sharing valence electrons to achieve the same configuration as the nearest rare gas. All rare gases (except He) have eight valence electrons, this observation is called the **octet rule**. The view of covalent bonding just described implies that each unpaired valence electron in the Lewis structure of an isolated atom is available

for sharing with another atom to form one bond. For example, the number of unpaired electrons on an atom of Groups 4A through 8A is just 8 minus the group number. (The number of unpaired electrons is equal to the group number for Groups 1A to 3A, but these elements, except boron, usually form ionic rather than covalent compounds.) For example, oxygen in Group 6A has $8 - 6 = 2$ unpaired electrons and forms 2 bonds.

2. IONIC BOND

One type of chemical bond is the ionic bond in which electrons are completely transferred from one atom to another. The formation of an ionic bond takes place in the reaction between the atom of low ionization energy with an atom of high electron affinity. An example of such a reaction is the reaction between sodium atoms and chlorine. A sodium atom has a low ionization energy: i.e. not much energy is required to pull off the outer electron.

A chlorine atom has a high electron affinity: i.e. considerable energy is released when an electron is added to its outer shell. Suppose these two atoms come together.

As shown in figure 10 sodium initially has one valence electron, and chlorine has seven.

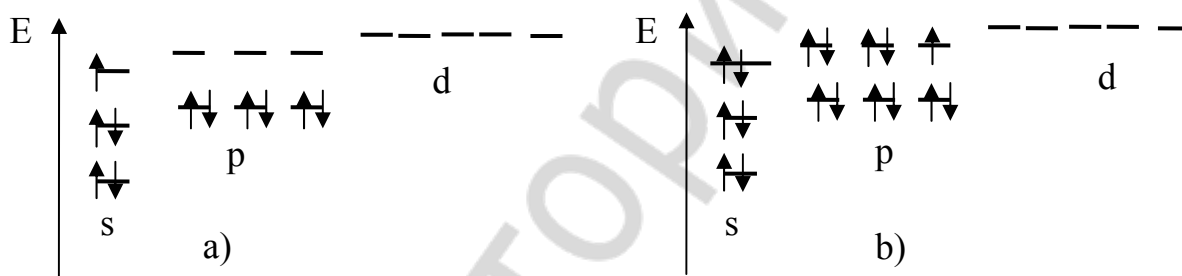
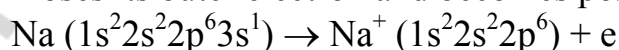


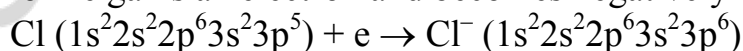
Fig. 10. Formation of an ionic bond: a – sodium atom, b – chlorine atom

In case when electron transfer, chlorine has eight valence electrons. The chlorine has a negative charge because of the gain of an electron. Now the sodium has a positive charge because of the loss of a negative electron. Thus, a positive ion and a negative ion are formed. Because the ions have opposite electric charges, they attract each other to produce an ionic bond. The formation of an ionic bond has three steps:

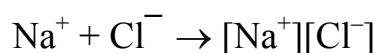
Step 1. Sodium loses its outer electron and becomes positively charged



Step 2. Chlorine gains an electron and becomes negatively charged



Step 3. Sodium and chlorine ions combine and NaCl is formed



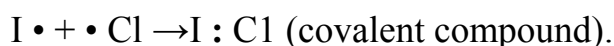
Since, in general, the elements on the left of the periodic table have low ionization potentials and the elements on the right have high electron affinity, mainly ionic bonds are formed (in reactions between these elements).

3. CHEMICAL BOND FORMATION

In case of a ionic bond where metals from the left side of the periodic table interact with nonmetals from the far right side, the result is usually the complete transfer of one or more electrons from one atom to another and the creation of an ionic bond.



When the elements lie closer in the periodic table, electrons are more often shared between atoms and the result is a covalent bond.



When two atoms approach each other closely enough for their electron clouds to interpenetrate, the electrons and nuclei repel each other; at the same time each atom's electrons attract the other atom's nucleus. If the total attractive force is greater than the total repulsive force, a covalent bond is formed (figure 11).

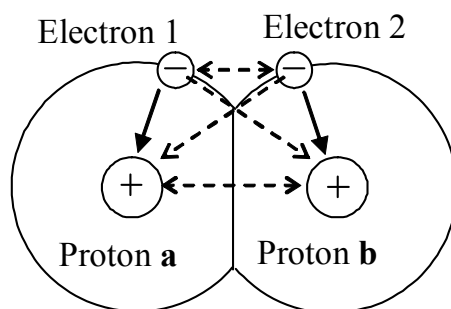


Fig. 11. The formation of a covalent bond in H_2 molecule. Pair of electrons (one electron from each atom) flows into the internuclear region and is attracted to both nuclei. It is this mutual attraction of 2 (or sometimes 4 or 6) electrons by two nuclei that leads to a force of attraction between two atoms and assists in bond formation

The second view of bonding, based on quantum mechanics, is more adaptable to mathematical analysis, but a bit harder to visualize. Here we imagine combining an atomic orbital from each of the two atoms to form a **bond orbital**.

Like an atomic orbital, a bond orbital can describe either one or two electrons; if there are two electrons (a bond pair) in a bond orbital, they must be paired with opposite spins. All the valence electrons of the atoms not involved in bonding are described by lone-pair orbitals, which are concentrated outside the bond region. The more the attraction between the bonding electrons and the nuclei exceeds the repulsion between the nuclei and between lone electron pairs, the stronger the bond will be between the atoms. Of course, a stronger bond means a more stable molecule with a lower potential energy.

The diagram in figure 12 shows the energy changes as a pair of electrons initially associated with separate H atoms becomes a bonding pair in H_2 .

The energy of the electrons in a bond orbital, where the electrons are attracted by two nuclei, is lower than their energy in valence atomic orbitals. There is also a quantum mechanical effect related to the size of the bond region compared to the size of the atomic orbital; because the electron is free to move in a larger space, its kinetic energy is lower. This effect is quite important in explaining certain types of bonds but we shall not explore it further.

Thus, in general, electrons fall to a lower potential energy when they become bonding electrons, and this energy is given off in the form of heat and/or light.

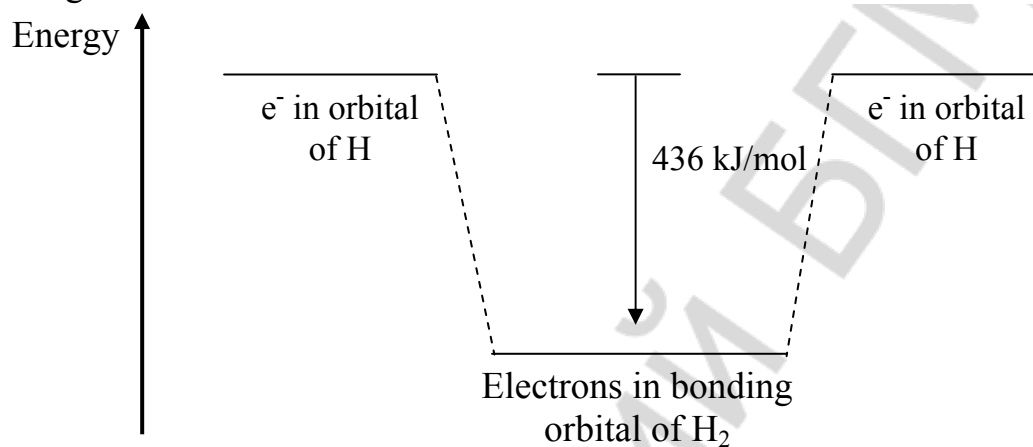


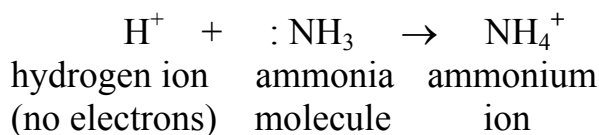
Fig. 12. Energy changes occurring in the process of bond formation between two H atoms

4. PROPERTIES OF COVALENT BOND

4.1. Single and multiple bonds. Molecules H-H, H-Be-H, H-O-H have a single pair of electrons (a **single** bond) between atoms. Single bonds are also called sigma bonds, symbolized by the Greek letter σ . Other structures, for example $\text{H}_2\text{C}=\text{CH}_2$, $\text{N}\equiv\text{N}$ indicate two or three electron pairs (a multiple bond) between the same pair of atoms. In a double or triple bond, one of the bonds is a sigma bond, but the second (and third if present) is a pi bond, denoted by the Greek letter π . Multiple bonds are most often formed by C, N, O and S atoms.

4.2. The donor-accepter mechanism of formation of covalent bond. In all of the compounds shown so far each atom contributes one unpaired electron to a bond pair, as in $\text{H}\cdot + \cdot\text{H} \rightarrow \text{H}:\text{H}$

Some elements, such as nitrogen and phosphorus, tend to share a lone pair with another atom that is short of electrons, leading to the formation of a coordinate covalent bond:



Once such a bond is formed, it is the same as any other bond; in the ammonium ion, for instance, all four bonds are identical.

4.3. The bond order. The bond order is the number of bonding electron pairs shared by two atoms in a molecule. Various molecular properties can be understood by this concept, including the distance between two atoms (bond length) and the energy required to separate the atoms from each other (bond energy).

BOND ORDER = 1. The bond order is 1 when there is only a sigma bond between the two bonded atoms. Examples are the single bonds in the following molecules. H—H F—F H—N in NH₃ H—C in CH₄

BOND ORDER = 2. The order is 2 when there are two shared pairs between two atoms. One of these pairs forms a sigma bond and the other pair forms a pi bond. Examples are the C=O bonds in CO₂ and the C=C bond in ethylene, C₂H₄.

BOND ORDER = 3 An order of 3 occurs when two atoms are connected by one sigma bond and two pi bonds. Examples are the carbon-carbon bond in acetylene (C₂H₂), the carbon-oxygen bond in carbon monoxide (CO), and the carbon-nitrogen bond in the cyanide ion (CN⁻).

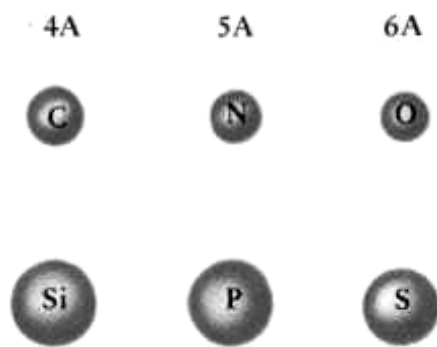
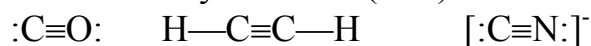
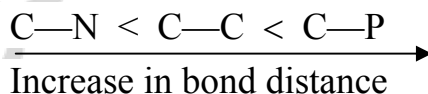


Fig. 13. Relative Atom Sizes for Groups 4A, 5A, and 6A

4.4. Bond length. The most important factor determining **bond length**, the distance between two bonded atoms, is the sizes of the atoms themselves. For given elements, the order of the bond then determines the final value of the distance. Atom sizes vary in a fairly smooth way with the position of the element in the periodic table (figure 13).

When you compare bonds of the same order, the bond length will be greater for the larger atoms. Thus, bonds involving carbon and another element would increase in length along the series



Similarly, a C=O bond will be shorter than a C=S bond, and a C≡N bond will be shorter than a C≡C bond.

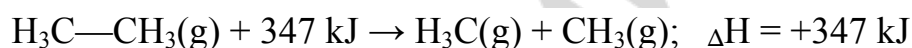
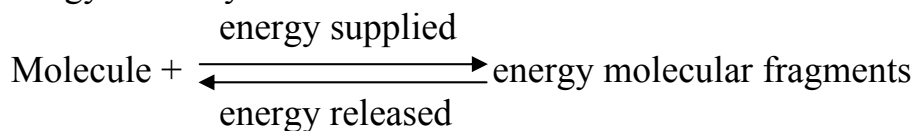
The effect of bond order is evident when you compare bonds between the same two atoms. For example, the bonds become shorter as the bond order increases in the series C—O, C=O, and C≡O.

Bond	C—O	C=O	C≡O
Bond Order	1	2	3
Bond Length (pm)	143	122	113

Adding a pi bond to the sigma bond in C—O shortens the bond by only 21 pm on going to C=O, rather than reducing it by half as you might have expected. The second pi bond results in a 9 pm reduction in bond length from C=O to C≡O.

4.5. Bond energy. The greater the number of bonding electron pairs between a pair of atoms, the shorter the bond. This implies that atoms are held together more tightly when there are multiple bonds, and so it should not be surprising that there is a relation between the bond order and the energy required to separate atoms.

Suppose you wish to separate, by means of chemical reactions, the carbon atoms in ethane (H₃C—CH₃), ethylene (H₂C=CH₂), and acetylene (HC≡CH) for which the bond orders are 1, 2, and 3, respectively. For the same reason that the ethane C—C bond is the longest of the series, and the acetylene C≡C bond is the shortest, the separation will require the least energy for ethane and the most energy for acetylene.



The energy that must be supplied to a gaseous molecule to separate two of its atoms is called the **bond dissociation energy** (or **bond energy** for short) and is given the symbol E_b . As E_b represents energy supplied to the molecule from its surroundings, E_b has a positive value, and the process of breaking bonds in a molecule is always endothermic. The amount of energy supplied to break the carbon-carbon bonds in the molecules above must be the same as the amount of energy released when the same bonds form. The formation of bonds from atoms in the gas phase is always exothermic. This means, for example, that ΔH for the formation of H₃C—CH₃ from two CH₃(g) fragments is -347 kJ/mol.

4.6. Polarity and electronegativity. Oxidation numbers. Covalent bonds are classified as polar or nonpolar. For example, the bonds in H₂ and Cl₂ are called nonpolar the bonds in HCl are polar. Not all atoms hold onto their valence electrons with equal strength. The elements all have different values of ionization energy and electron affinity. If two different elements form a bond, the one with higher electronegativity will attract the shared pair more strongly than the other. Only when two atoms of the same kind form a bond can we presume that the bond pair is shared equally between the two atoms.

In H₂ and Cl₂ the «center of gravity» of the negative-charge distribution is at the center of the molecule, since the shared pair is distributed equally over the two atoms. In H₂ and Cl₂ contain an equal number of positive and negative charges (protons and electrons). Also the center of the positive charge coincides

with the center of the negative charge. The molecule is a nonpolar molecule; it contains a nonpolar bond because an electron pair is shared equally between two atomic kernels. In case of HCl, the bond is called polar because the center of positive charge does not coincide with the center of negative charge. The formation of hydrogen chloride can be expressed as follows: $\text{H}\cdot + \cdot\text{Cl} = \text{H}:\text{Cl}$

Although chlorine has a greater attraction for electrons than hydrogen, the HCl bond is not the ionic bond. Instead, there is a covalent bond arising from electron sharing of the odd electrons of the two atoms, the 1s of the H and the 3p of the Cl. The molecule as a whole is electrically neutral, because it contains an equal number of positive and negative charges. However, owing to the unequal sharing of the electron pair, the molecule chlorine end is negative, and the hydrogen end is positive. Because H and Cl are different atoms, the sharing of electrons is unequal. This arises because, the bonding electrons spend more time on the chlorine atom than on the hydrogen atom.

Thus, there is a fundamental difference between a single bond in HCl and a single bond in H_2 or Cl_2 . We usually indicate polarity by using the symbols δ^+ and δ^- , which indicate partial + and - charges. Some polar bonds in common molecules are HF, H_2O , NH_3 .

The electrical charge on a free atom is zero. If the atom is bound to another in a molecule, however, it is impossible to say what its charge may be, since some valence electrons are shared with other atoms. It is possible, though, to define the limiting case to determine at least the sign and maximum value of the charge on an atom involved in a bond. This limiting situation arises if we agree that all the bond pair electrons belong to the more electronegative atom in a bond, which amounts to assuming that all bonds are ionic. The charge on the atom calculated in this «ionic limit» is called the oxidation number.

Here you see that the oxidation number is given by the number of electrons acquired by the atom in excess of its valence electrons (negative oxidation number) or the number released by the atom (positive oxidation number) in the ionic limit.

4.7. Molecular Shape. Molecular polarity. Lewis structures only show how many bond pairs and lone pairs surround a given atom. However, all molecules are three dimensional, and most molecules have their atoms in more than one plane in space. It is often important to know the way molecules fill space, because the structure partly determines the chemical functioning of the molecule. Pharmaceutical companies, for example, use knowledge of molecular shape to design drugs that will fit into the site in the body where pain is to be relieved or disease attacked.

To convey a sense of three dimensionality for a molecule drawn on a piece of flat paper, we use sketches such as a «ball-and-stick» model of methane, or we can draw structures in perspective using «wedges» for bonds that emerge from or recede into the plane of the drawing. A sampling of perspective

sketches and ball-and-stick models of molecules for which we have already drawn Lewis structures is shown in table 6. Although you do not yet know how to predict the structures in this table there is an easy way to do it. Notice how the molecular shape changes with the number of sigma bonds plus lone pairs about the central atom.

Sigma bonds + lone pairs on central atom	Structure of molecule in table 6
2	Linear
3	Trigonal planar
4	Tetrahedral (or pyramidal)
5	Trigonal bipyramidal
6	Octahedral

The idea that will allow us to predict the molecular structure is that each lone pair or bond group (sigma + pi pairs) repels all other lone pairs and bond pair groups. Because the pairs try to avoid one another, they move as far apart as possible, and, since all of the pairs are «tied» to the same central atom nucleus, they can only orient themselves so as to make the angles between themselves as large as possible (figure 14).

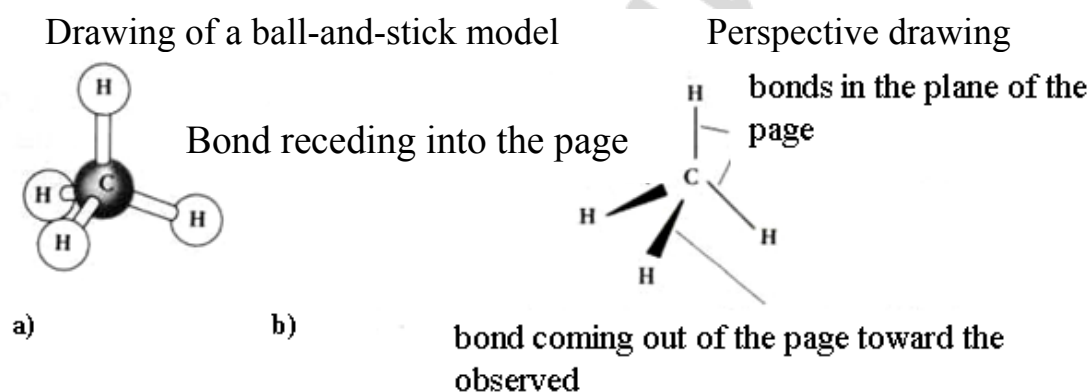


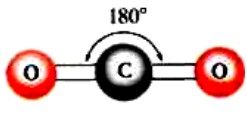
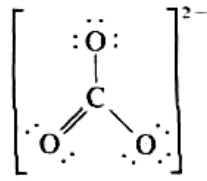
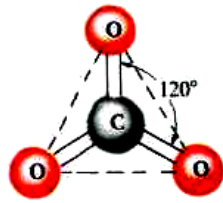
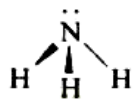
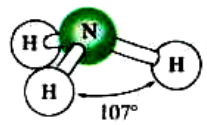
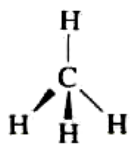
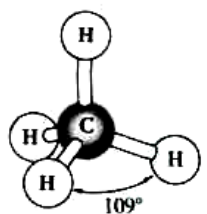
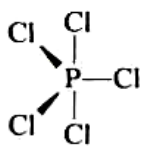
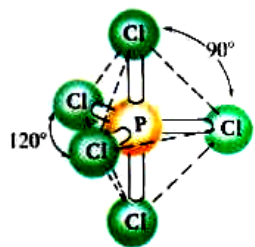
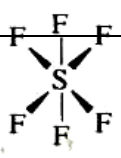
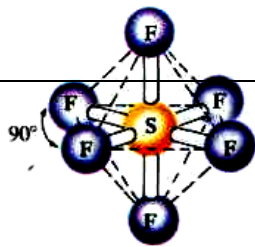
Fig. 14. The structure of methane, CH₄, to show the ways molecular structures will be illustrated: a – drawing of a ball-and-stick model; b – perspective drawing

The adjective «polar» was used in point 4.6. To describe the situation of separated positive and negative charges in a bond. However, because most molecules have at least some polar bonds, molecules can themselves be polar. In a polar molecule, there is an accumulation of electron density toward one side of the molecule, so that one end of the molecule bears a slight negative charge, δ^- ; the other end has a slight positive charge of equal value, δ^+ . The experimental measure of this separation of charge is the molecule's dipole moment, which is defined as the product of the size of the charge (δ) and the distance of separation. The units of dipole moment are therefore coulomb • meters; a convenient unit is the debye (D), defined as $1 \text{ D} = 3.34 \times 10^{30} \text{ C} \cdot \text{m}$. Polar molecules will align themselves with an electric field, and they will also

align themselves with each other. This interaction of polar molecules is an extraordinarily important effect in water and other substances.

Table 6

Perspective Molecular Sketches

Molecule	Geometry	Perspective sketch	Ball-and-stick model
CO ₂	Linear	O=C=O	
CO ₃ ²⁻	Trigonal planar		
NH ₃	Pyramidal		
CH ₄	Tetrahedral		
PCl ₅	Trigonal bipyramidal		
SF ₄	Octahedral		

--	--	--	--

5. THEORIES OF CHEMICAL BONDING

There are two commonly used approaches to chemical bonding: the **valence bond (VB) theory** and the **molecular orbital (MO) theory**. The former was first developed by Linus Pauling, while the latter by Robert Mullikan. Mullikan's approach is to combine pure atomic orbitals on each atom to derive *molecular orbitals* that are spread or **delocalized** over the molecule. Only after developing the molecular orbitals are the pairs of electrons of the molecule assigned to these orbitals; thus, the molecular electron pairs are more or less uniformly distributed over the molecule. In contrast, Pauling's approach is more closely tied to Lewis's idea of electron pair bonds, where each electron pair is confined to the space between two bonded atoms and of lone pairs of electrons localized on a particular atom. Only bonding and nonbonding (lone pair) orbitals are considered.

5.1. The Valence Bond theory. According to this theory, two atoms form a bond when both of the following conditions occur:

1. There is the **orbital overlap** between the two atoms (figure 15). If two H atoms approach each other closely enough, their 1s orbitals can partially occupy the same region of space.

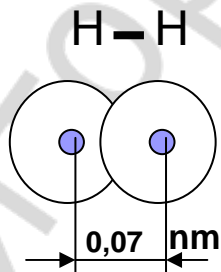


Fig. 15. The orbital overlap between the two H atoms

2. A maximum of two electrons, of the opposite spin, is present in the overlapping orbitals. Due to orbital overlap, the pair of electrons is found within a region influenced by both nuclei. This means that both electrons are mutually attracted to both atomic nuclei, and this, among other factors, leads to bonding.

As the extent of overlap between two orbitals increases, the strength of the bond increases. This is seen in figure 16 as a drop in energy as two H atoms, originally far apart, come closer and closer together.

However, the figure also shows that, as the atoms come very close to one another, the energy increases rapidly, due to the repulsion of one positive

nucleus by the other. Thus, there is an optimum distance, the observed bond distance, at which the total energy is a minimum; here there is a balance of attractive and repulsive forces.

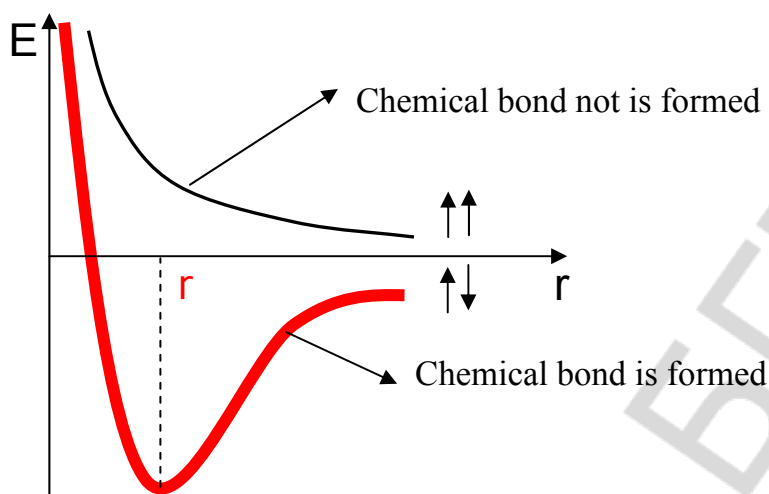


Fig. 16. Total potential energy change in the course of H–H bond formation

The overlap of two s orbitals, one from each of two atoms leads to a **sigma bond**: the electron density of a sigma bond is the greatest along the axis of the bond figure 17. Sigma bonds can also form by the overlap of an s orbital with a p orbital or by the head-to-head overlap of two p orbitals.

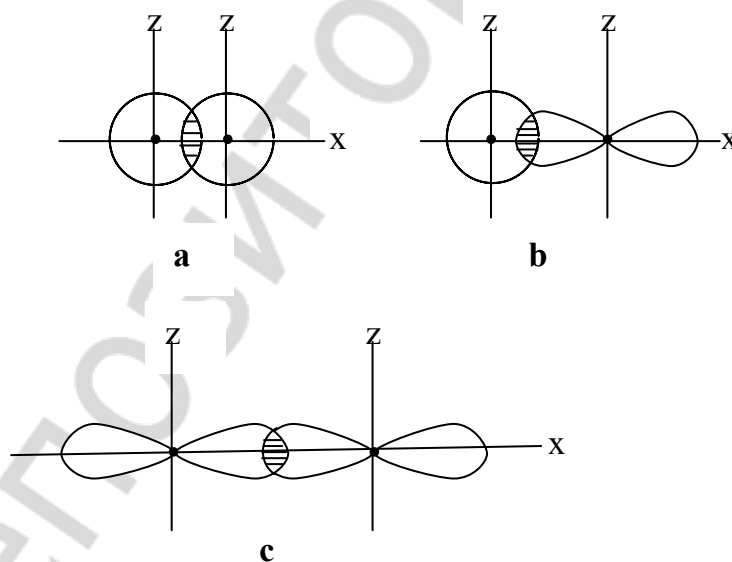
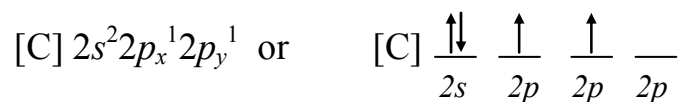


Fig. 17. The formation of σ -bond:

a) s – s; b) s – p; c) p_x – p_x

Hybrid orbitals. An isolated carbon atom has two unpaired electrons, and so might be expected to form only two bonds.

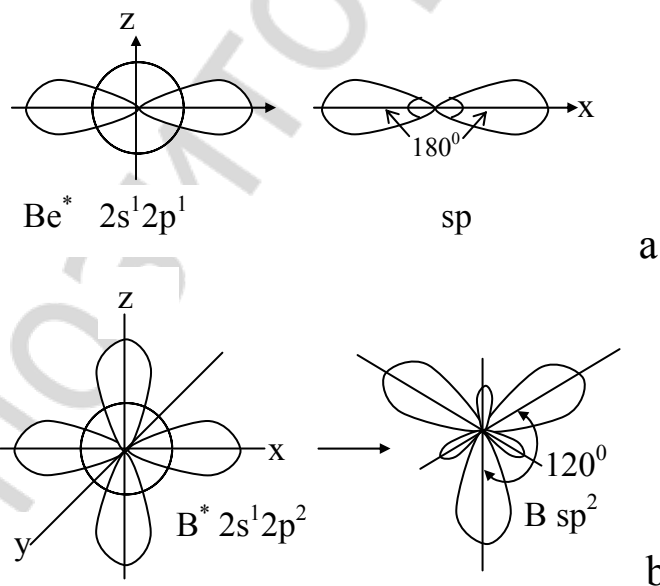
Carbon Electron Configuration



However, there are four C–H bonds in methane and the geometry of the C atom in CH₄ is tetrahedral. There must be *four equivalent* bonding electron pairs around the C atom. The three *p* orbitals around an isolated atom lie at the angle of 90° to one another. Therefore, if sigma bonds were formed in some manner using pure *s* and *p* orbitals, the bonds would neither be equivalent nor would they be arranged correctly in space. Some other scheme is required to account for C–H bonds at an angle of 109° (table 6).

Pauling proposed **orbital hybridization** as a way to explain the formation of bonds by the maximum overlap of atomic orbitals and yet accommodate the use of *s* and *p* orbitals. In order for the four C–H bonds of methane to have their maximum strength, there must be maximum orbital overlap between the carbon orbitals and the H-atom *s* orbitals at the corners of a tetrahedron. Thus, Pauling suggested that the approach of the H atoms to the isolated C atom causes distortion of the four carbon *s* and *p* orbitals. These orbitals **hybridize** or combine in some manner to provide *four equivalent hybrid orbitals that point to the corners of a tetrahedron*.

We label each hybrid orbital as **sp³**, since the orbitals are the result of the combination of one *s* and three *p* orbitals on one atom (figure 18). Each hybrid orbital combines the properties of its *s* and *p* orbital parents.



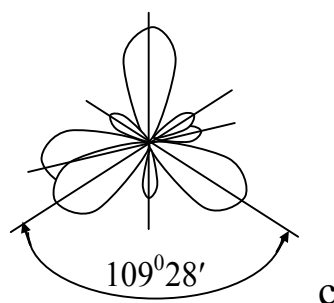


Fig. 18. Types of orbital hybridization;
 a – sp -hybridization; b – sp^2 -hybridization; c – sp^3 -hybridization

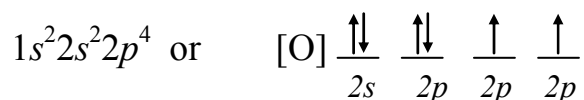
The theory of orbital hybridization is an attempt to explain how in CH_4 for example, there can be four equivalent bonds directed to the corners of a tetrahedron. Another outcome of hybrid orbital theory is that hybrid orbitals are more extended in space than any of the atomic orbitals from which they are formed. This important observation means that greater overlap can be achieved between C and H in CH_4 , for instance, and stronger bonds result than without hybridized orbitals.

The four sp^3 hybrid orbitals have the same shape, but they differ in their direction in space. Each also has the same energy, which is the weighted average of the parent s and p orbital energies. Four sigma bonds are to be formed by carbon, so each of the four valence electrons of carbon is assigned, according to Paul's principle and Hund's rule, to a separate hybrid orbital.

Overlap of each half-filled sp^3 hybrid orbital with a half-filled hydrogen $1s$ orbital gives *four equivalent C–H bonds arranged tetrahedrally*, as required by experimental evidence.

Hybrid orbitals can also be used to explain bonding and structure for such common molecules as H_2O and NH_3 . An isolated O atom has two unpaired valence electrons as required for two bonds, but these electrons are in orbitals 90° apart.

Oxygen Electron Configuration



However, we know that the water molecule is based on an approximate tetrahedron of structural pairs: the two bond pairs are 105° apart, and the lone pairs occupy the other corners of the tetrahedron (figure 19). If we allow the four s and p orbitals of oxygen to distort or hybridize on approach of the H atoms, four sp^3 hybrid orbitals are created. Two of these orbitals are occupied by unpaired electrons, and lead to the O–H sigma bonds. The other two orbitals contain pairs of electrons and so are the lone pairs of the water molecule.

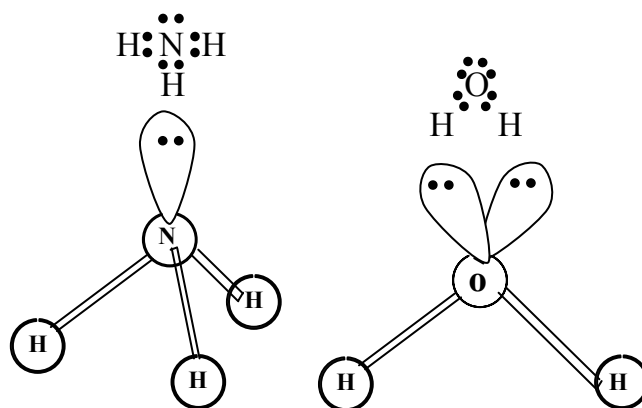


Fig. 19. Orbital hybridization in H_2O and NH_3 molecules

5.2. Molecular Orbital theory. Molecular orbital (MO) theory is an alternative way to view electron orbitals in molecules. In contrast to the localized bond and lone pair orbitals of valence bond theory, pure s and p atomic orbitals of the atoms in the molecule combine to produce orbitals that are spread or delocalized over several atoms or even over the entire molecule. The new orbitals are called *molecular orbitals*, and they can have different energies. Just as with orbitals in atoms, molecular orbitals are assigned to electrons according to the Pauli principle and the Hund's rule.

One reason for learning about the MO concept is that it correctly predicts the electronic structures of certain molecules that do not follow the electron-pairing assumptions of the Lewis approach. The most common example is the O_2 molecule. The electron dot structure of the molecule as $:\ddot{\text{O}} = \ddot{\text{O}}:$, with all electrons paired. However, experiments clearly show that the O_2 molecule is *paramagnetic* and that it has exactly two unpaired electrons per molecule. It is sufficiently magnetic that solid O_2 clings to the poles of a magnet. The molecular orbital approach can account for the paramagnetism of O_2 more easily than the valence bond theory. To see how MO theory can be applied to O_2 and other small diatomic molecules, we shall first describe *four principles* of the theory.

Principles of molecular orbital theory. The **first principle** of molecular orbital theory is that the number of molecular orbitals produced is *always* equal to the number of atomic orbitals brought by the combining atoms. To see the consequences of this, consider first the H_2 molecule.

Bonding and antibonding molecular orbitals in H_2 . When the $1s$ orbitals of two atoms overlap, two molecular orbitals are obtained. The principles of molecular orbital theory tell us that, in one of the resulting molecular orbitals, the $1s$ regions of electron density *add* together to lead to an increased probability that electrons are found in the bond region. Thus, electrons in such an orbital attract both nuclei. Since the atoms are there by bound together, the molecular orbital is called a **bonding molecular orbital**. Moreover, it is a sigma orbital, since the region of electron probability lies directly along the bond axis. We label this molecular orbital σ_{1s} .

Since two combining atomic orbitals *must* produce two molecular orbitals, the other combination is constructed by *subtracting* one orbital from the other. When this happens there is reduced electron probability *between* the nuclei for the molecular orbital. This is called an **antibonding molecular orbital**. Since it is also a sigma orbital, it is labeled σ^*_{1s} , where the asterisk conveys the notion of an antibonding orbital.

A **second principle** of molecular orbital theory is that the bonding molecular orbital is lower in energy than the parent orbitals, and the antibonding orbital is higher in energy (figure 20). The average energy of the molecular orbitals is slightly higher than the average energy of the parent atomic orbitals.

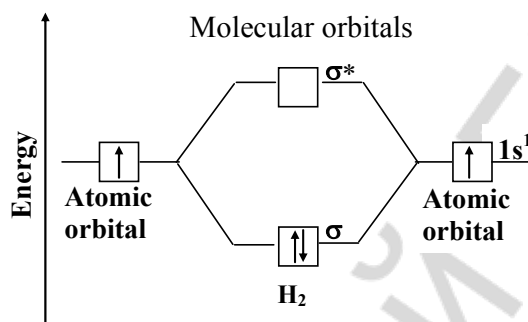


Fig. 20. Bonding and antibonding molecular orbitals in H_2

A **third principle** of molecular orbital theory is that the electrons of the molecule are placed in orbitals of successively higher energy; the Pauli principle and the Hund's rule are obeyed. Thus, electrons occupy the lowest energy orbitals available, and they do so with spins paired. Since the energy of the electrons in the bonding orbital of H_2 is lower than that of either parent $1s$ electron, the H_2 molecule is stable. We write the electron configuration H_2 as $(\sigma_{1s})^2$.

Next consider putting two helium atoms together to form He_2 . Since both He atoms have $1s$ valence orbitals, they combine to produce the same kind of molecular orbitals as in H_2 . The four helium electrons are assigned to these orbitals according to the scheme shown in figure 21. The pair of electrons in σ_{1s} stabilizes He_2 . However, the two electrons in σ^*_{1s} destabilize the He_2 molecule a little more than the two electrons in σ_{1s} stabilize He_2 . Thus, molecular orbital theory predicts that He_2 has no net stability, and laboratory experiments indeed show that two He atoms have little tendency to combine.

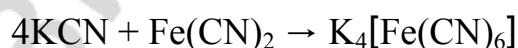
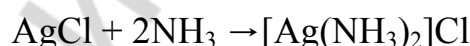
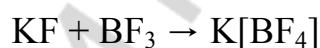
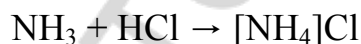
σ_{2p}					
π_{2p}					
$\sigma_{2x}^* S$					
$\sigma_{2x} S$					
Bond order	One	Two	Three	Two	One
Bond-dissociation energy (kJ/mol)	290	620	941	495	155
Bond distance (pm)	159	131	110	121	143

The molecular orbital electron configuration for O_2 clearly shows that the bond order is two. Hund's rule requires two unpaired electrons, exactly as determined by experiment. Thus, a simple molecular orbital picture leads to a reasonable view of the bonding in paramagnetic O_2 , a point on which simple valence bond theory failed.

Finally, molecular orbital theory predicts the bond order of F_2 to be one, and the molecule does indeed have the weakest bond of the series in table 7.

CHAPTER III Complex (coordination) compounds

Common chemical compounds are built according to the rules of valence: NH_3 , H_2O , HCl , HF , $AgCl$, BF_3 and so on. These compounds are relatively simple. They can react with each other producing more complex compounds.



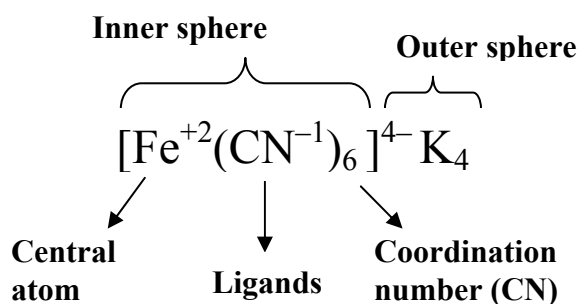
Such compounds got the name of complex (coordination) compounds.

Complex compounds are the compounds where in the nodes of their lattice there are complex ions or neutral complex particles, which can exist either in solutions or in fluxes. The reactions in the result of which these complex compounds are formed are called the **complexation reactions**.

The first theory of the structure of complex compounds was devised by Alfred Verner in 1893.

We should differentiate the inner coordination sphere and the outer sphere. The inner coordination sphere is the aggregate of the central atom (complex former) and the ligands (molecules or ions). The charge of the inner sphere equals the algebraic sum of the charges of the central atom and the ligands.

The inner sphere or a complex are enclosed in brackets. As an example let's have a look at the constituent parts of such complex compound as $K_4[Fe(CN)_6]$:



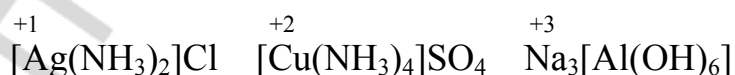
Atoms of a ligand which help to make bonds with the central atom are called **donor atoms**. The most frequently used ligands are those with donor atoms of oxygen, nitrogen and sulphur. The number of ligands participating directly in the bonding with the central atom is called the coordination number.

The outer sphere is the aggregate of all the ions situated outside the inner coordination sphere. The charge of the inner sphere is compensated by the ions of the outer sphere with the opposite sign. Usually the outer sphere consists of simple monatomic and polyatomic ions.

Any element of the periodic table can function as a central atom in the structure of the inner sphere. d- and f-elements show the highest complex forming ability, p-elements have somewhat lower ability and s-elements can function as a central atom very rarely. The central atom can have any oxidation number.



The value of the coordination number of the central atom depends on its nature, oxidation number, the nature of ligands and the conditions for the complexation reaction to take place. The value of the coordination number may vary in different complex compounds from 2 till 8 and higher. The most widespread coordination numbers are 4 and 6. **In most cases the value of the coordination number is twice as high as the oxidation number of the central atom.**



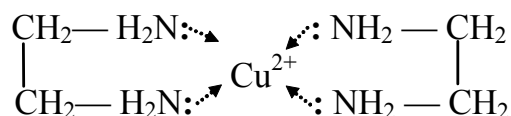
The greater is the charge of the central atom and the smaller is its radius, the more durable is the complex.

As ligands we can find ions and neutral molecules. The number of donor atoms of a ligand forming these coordination bonds with the central atom is called the **dentation** of a ligand. Depending on the number of donor atoms we can distinguish ligands with different dentation. If a ligand forms one coordination bond with the central atom, it's a **monodentate** ligand. The number of

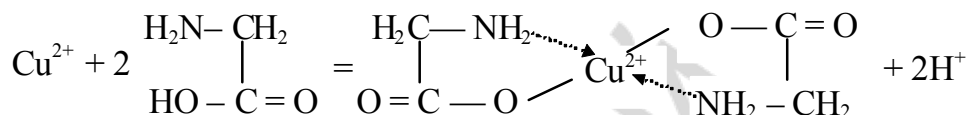
The inner coordination sphere is connected with the outer sphere by an ionic bond.

CYCLIC COMPLEXES OR CHELATES

Complexes with polydentate ligands contain cycles which include the central atom. Such complexes are called **chelates**. The example of such complex can be ethylenediamine copper (II) complex:



The group of chelates also includes the inner complex compounds which have the central atom linked with ligands by a covalent bond formed according to donor-acceptor and exchange mechanisms. The formation of the inner complex compounds is accompanied by the substitution of one or several protons from the acid functional groups by a metal ion.



The inner complex compounds are hemoglobin, chlorophyll, vitamin B₁₂, many enzymes and other biologically active compounds.

CLASSIFICATION AND NOMENCLATURE OF COMPLEX COMPOUNDS

I. According to the charge of the inner sphere the complexes can be:

Cationic: [Ag(NH₃)₂]⁺Cl diamminesilver (I) chloride; [Cu(NH₃)₄]²⁺SO₄ tetraamminecopper (II) sulphate.

Anionic: K₄[Fe(CN)₆]⁴⁻ potassium hexacyanoferrate (II); K[Pt(NH₃)Cl₃]⁻¹ potassium amminetrichlorplatinate (II).

Neutral: [Co(NH₃)₃Cl₃]⁰ trichlorotriamminecobalt; [Fe⁰(CO)₅]⁰ pentacarbonyl iron.

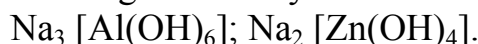
II. This classification of complex compounds is based on the nature of ligands.

Acidocomplexes. As ligands are the acid residua Cl⁻ (chloro); CN⁻ (cyano); CNS⁻ (rhodanic); NO₂⁻ (nitro); SO₄²⁻ (sulphate) and so on.

Aminocomplexes (ammines). As ligands are the ammonia molecules: [Cu(NH₃)₄]SO₄; [Cr(NH₃)₆]Cl₃; [Pt(NH₃)₆]Cl₄.

Aquacomplexes. As ligands are the molecules of water: [Co(H₂O)₆]Cl₂; [Cr(H₂O)₆]Cl₃.

Hydroxocomplexes. As ligands are hydroxide ions OH⁻:



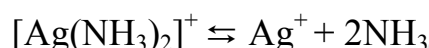
Carbonyl complexes. In **carbonyl** complexes CO-ligands are covalently bonded with the help of carbon atom with the metal having zero oxidation number: [Ni(CO)₄]; [Fe(CO)₅].

DISSOCIATION OF COMPLEX COMPOUNDS IN SOLUTIONS

The inner and the outer spheres of a complex compound differ greatly according to the stability.

Particles, situated in the outer sphere, are bound with a complex ion by electrostatic forces and can easily dissociate in water solution. Ligands, situated in the inner sphere, are more firmly bonded with the central atom and dissociate to a smaller extent. That's why the dissociation of complex compounds has two stages. At the first stage the dissociation occurs as the dissociation of strong electrolytes: $[\text{Ag}(\text{NH}_3)_2]\text{Cl} \rightarrow [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$

At the second stage the dissociation occurs as the one of weak electrolytes, it's reversible and partial:



The ion dissociation $[\text{Ag}(\text{NH}_3)_2]^+$ like the dissociation of any weak electrolyte is expressed by the constant of chemical equilibrium:

$$K_{\text{ch.e.}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[[\text{Ag}(\text{NH}_3)_2]^+]} = K_i$$

The constant of chemical equilibrium $K_{\text{ch.e.}}$ in case of the dissociation of a complex ion is called **the constant of instability K_i** . It characterizes the stability of the inner sphere of complex compounds. **The less is K_i** , the less is the concentration of decay products of the complex and **the more stable is the complex**.

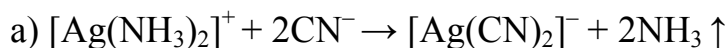
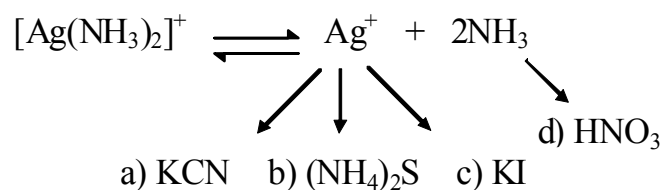
To characterize the stability of complex compounds you can use the value inverse to the constant of instability which is called the **constant of stability K_s** .

$$K_s = \frac{1}{K_i} = \frac{[[\text{Ag}(\text{NH}_3)_2]^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

The greater is K_s , the more stable is the complex.

DESTRUCTION OF COMPLEX COMPOUNDS

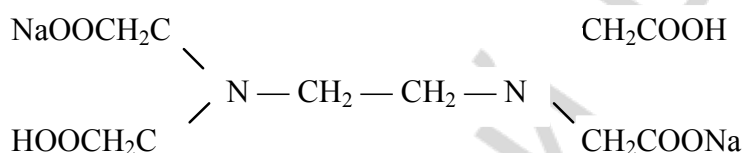
To destroy a complex you should shift the equilibrium of dissociation of the inner sphere to the right. This can be achieved by the formation of a more stable complex, an almost insoluble precipitate, a weak electrolyte or a gaseous product. For example, the equilibrium of ion dissociation $[\text{Ag}(\text{NH}_3)_2]^+$ can be shifted to the right by binding of Ag^+ or NH_3 :



- $K_i. [Ag(CN)_2]^- = 1 \cdot 10^{-21} < K_i. [Ag(NH_3)_2]^+ = 6,8 \cdot 10^{-8}$
 b) $2[Ag(NH_3)_2]^+ + (NH_4)_2S \rightarrow Ag_2S \downarrow + NH_4^+ + 4 NH_3 \uparrow$
 c) $[Ag(NH_3)_2]^+ + KI \rightarrow AgI \downarrow + 2NH_3 \uparrow + K^+$
 d) $[Ag(NH_3)_2]Cl + 2HNO_3 = AgCl \downarrow + 2NH_4NO_3$

EQUILIBRIA AND THE PROCESSES IN SOLUTIONS WITH COMPLEX COMPOUNDS

In a human body there is a constant process of destruction and formation of biocomplexes from the cations of biometals (iron, copper, zinc, cobalt) and bioligands (porphyrins, aminoacids, proteins, polypeptides, nucleic acids, ATP). The study of the processes taking place in the organism to form complex compounds can be of great importance for prevention and treatment of a number of diseases. For example, chelators such as polyaminocarbonic acids and



their salts are widely used for the excretion of ions of toxic metals from the organism. In medicine there is a special trend connected with the usage of complexons which is called **chelation therapy**. The disodium salt of ethylenediaminetetraacetic acid (EDTA or complexon III, trade name trilon B) has got a wide distribution.

With the help of this salt it's possible to increase the excretion of ions of toxic metals such as lead, mercury, cadmium and barium and others from the organism. The formed complex compounds are soluble in water, are not degraded in biological medium and can be easily excreted through the kidneys. The ability to form stable complex compounds with many metals can be seen in many other calcium and cobalt salts of EDTA. For example, calcium salt is widely used in cases of poisoning with lead.

Proteins are polydentate ligands and can easily combine with heavy metals. When poisoned with the salts of heavy metals the patient is given some milk and fresh eggs which contain lots of proteins. The formed complex compounds aren't absorbed by the blood of the intestine and heavy metals are excreted in such a way.

Vitally important elements Zn, Cu, Fe, Mn, Co, Mo are part of some enzymes called metalloenzymes. The most well-known are carbonic anhydrase, xanthine oxidase, cytochromes which have zinc, molybdenum and iron in their active centres. Ligands in metalloenzymes are the proteins and their central atoms are the ions of metals.

CHAPTER IV

Heterogeneous equilibria

Heterogeneous equilibria are the equilibria in the heterogeneous systems. Heterogeneous systems consist of several phases separated by real physical borders of phase divisions. The examples of these systems are gas-liquid, solid-liquid, solid-gas. Heterogeneous systems are always multiphase. *Phase* is a part of a system with identical chemical and physical properties.

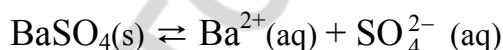
THE SOLUBILITY CONSTANTS

Let's consider a heterogeneous system which consists of a slightly soluble precipitate of a strong electrolyte and a saturated solution over it when they both are in dynamic chemical equilibrium. When the precipitate (e.g. BaSO₄) contacts with water there are two processes in this system:

1) dissolution when polar water molecules transfer a part of ions from the ionic lattice of BaSO₄ into a liquid phase;

2) precipitation when under the influence of electrostatic field of BaSO₄ lattice a part of Ba²⁺ and SO₄²⁻ ions transfers from its liquid phase into a solid one building up the lattice of the salt.

With time the dissolution rate will become equal to the precipitation rate and there will be the dynamic equilibrium between the crystalline precipitate of slightly soluble salt BaSO₄ and its water solution containing Ba²⁺ (aq) and SO₄²⁻ (aq) ions:



The solution being in the equilibrium with a solid phase which consists of BaSO₄ is called *saturated with respect to the precipitate*. Such a solution is the equilibrium heterogeneous system.

Let's apply the law of mass action to this equilibrium heterogeneous process. As BaSO₄ is a slightly soluble strong electrolyte, we'll use the apparent concentration (activity):

$$K_{\text{ch.e.}} = \frac{a_{\text{Ba}^{2+}(\text{aq})} \cdot a_{\text{SO}_4^{2-}(\text{aq})}}{a_{\text{BaSO}_4(\text{s})}}$$

In chemistry the activity **a** of a solid phase is taken as 1 and it is a constant. The product of these two constants gives a new constant called **the thermodynamic solubility constant and denoted by K_s⁰**:

$$a_{\text{BaSO}_4} = 1; \text{ then } \underbrace{K_{\text{ch.e.}} \cdot a_{\text{BaSO}_4(\text{s})}}_{K_s^0} = a_{\text{Ba}^{2+}(\text{aq})} \cdot a_{\text{SO}_4^{2-}(\text{aq})};$$

$$\text{i.e. } K_s^0 = a_{\text{Ba}^{2+}(\text{aq})} \cdot a_{\text{SO}_4^{2-}(\text{aq})}$$

So, in a saturated solution of a slightly soluble strong electrolyte the product of the equilibrium ion activities is a constant at a given temperature.

The solution being in the equilibrium with BaSO_4 precipitate is called saturated but strongly diluted. In saturated solutions of strong electrolytes the activity coefficient is $f_a \rightarrow 1$ and $a \rightarrow C$. In this case ion activities can be substituted by their molar concentrations and the thermodynamic solubility constant K_s^0 will become **the concentration solubility constant K_s** :

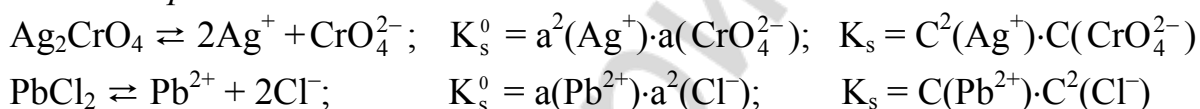
$$K_s = C(\text{Ba}^{2+}) \cdot C(\text{SO}_4^{2-}),$$

where C is the equilibrium anion and cation concentrations (mol/L) in a saturated solution of a strong electrolyte.

The molar concentrations of the ions involved in the equilibrium each raised to the power of its stoichiometric coefficient in the balanced equilibrium equation.

If a slightly soluble strong electrolyte forms several ions when dissociated, the ion activities (concentrations) in appropriate degrees are included into the equations K_s^0 and K_s .

Examples:



In general the thermodynamic and the concentration solubility constants for the reaction: $\text{A}_m\text{B}_n(\text{s}) \rightleftharpoons m\text{A}^{n+}(\text{aq}) + n\text{B}^{m-}(\text{aq})$ can be written as follows:
 $K_s^0 = a^m(\text{A}^{n+}) \cdot a^n(\text{B}^{m-}); K_s = C^m(\text{A}^{n+}) \cdot C^n(\text{B}^{m-})$

To simplify the calculations we can use the concentration solubility constant K_s taking $f_a = 1$ and $K_s = K_s^0$.

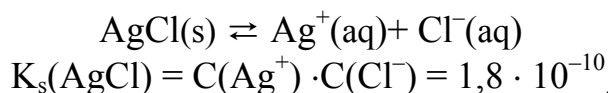
INTERCONNECTION BETWEEN SOLUBILITY AND K_s^0

The solubility of different substances is quantitatively expressed by the concentration of saturated solutions. So, *the solubility of a given substance is equal to its molar concentration in the saturated solution (molar solubility of a substance): S (mol/L). Solubility can also be expressed in grams of a solute per 100 gram of a solvent or in grams of a solute per 1 L of the solution.*

Solubility of solids depends on the nature of solute, solvent, temperature and so on.

The connection between the value K_s^0 and the solubility depends on the amount of ions which are the result of dissociation of a slightly soluble strong electrolyte in the solution. Let's consider some examples of how to calculate the molar solubility of a slightly soluble strong electrolyte using its value K_s taking into account that $K_s^0 = K_s$:

a) binary electrolyte:



In the state of equilibrium in accordance with the reaction condition:

$$C(\text{Ag}^+) = C(\text{Cl}^-) = S(\text{AgCl}).$$

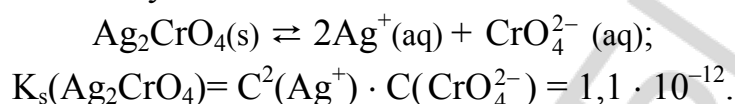
Let's express the value K_s of the salt in terms of the value of its solubility:

$$K_s(\text{AgCl}) = S^2(\text{AgCl}),$$

consequently,

$$S(\text{AgCl}) = \sqrt{K_s(\text{AgCl})} = \sqrt{1,8 \cdot 10^{-10}} = 1,3 \cdot 10^{-5} \text{ (mol/L)}.$$

b) three-ion electrolyte:



In the state of equilibrium in accordance with the reaction condition:

$$C(\text{CrO}_4^{2-}) = S(\text{Ag}_2\text{CrO}_4);$$

$$C(\text{Ag}^+) = 2S(\text{Ag}_2\text{CrO}_4).$$

Let's express the value K_s of the salt in terms of the value of its solubility:

$$K_s(\text{Ag}_2\text{CrO}_4) = (2S)^2 \cdot S = 4S^3(\text{Ag}_2\text{CrO}_4),$$

consequently,

$$S(\text{Ag}_2\text{CrO}_4) = \sqrt[3]{\frac{K_s(\text{Ag}_2\text{CrO}_4)}{4}} = \sqrt[3]{\frac{1,1 \cdot 10^{-12}}{4}} = 6,5 \cdot 10^{-5} \text{ (mol/L)}.$$

In general, the dependence between K_s and S of a slightly soluble strong electrolyte of type $\mathbf{A}_m\mathbf{B}_n$ can be expressed by the following equation:

$$S(\mathbf{A}_m\mathbf{B}_n) = \sqrt[m+n]{\frac{K_s(\mathbf{A}_m\mathbf{B}_n)}{m^m \cdot n^n}}$$

Comparing the value K_s^0 of single-type electrolytes (when dissolved, 1 mole of different slightly soluble strong electrolytes forms the same number of mole ions) it's possible to estimate qualitatively the solubility of precipitates.

Precipitate K_s^0 (25°C)

AgCl $1,8 \cdot 10^{-10}$

AgBr $5,3 \cdot 10^{-13}$

AgI $8,3 \cdot 10^{-17}$

Among the mentioned silver halogenides, AgI is the least soluble and AgCl is the most soluble.

Less the K_s^0 – less the solubility S of single-type electrolytes ($K_s^0 \approx K_s$).

CONDITIONS OF FORMATION AND SOLUBILIZATION OF PRECIPITATES

When ion concentration in the solution is known, we can suppose the direction of the heterogeneous process.

Let's imagine that we have an equilibrium heterogeneous system: $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$. In this system the solution will be saturated only if $C(\text{Ag}^+) \cdot C(\text{Cl}^-) = K_s$. In the other case the solution will not be saturated.

If $C(\text{Ag}^+) \cdot C(\text{Cl}^-) < K_s$ we can observe the dissolution of the precipitate or the equilibrium shift to the right in this heterogeneous system.

AgCl will precipitate when $C(\text{Ag}^+) \cdot C(\text{Cl}^-) > K_s$. So, the precipitate will fall out only in this case when the product of ion concentration of a slightly soluble strong electrolyte will be greater than the value of concentration solubility constant K_s .

So, the precipitation is a successive process which can be divided into 3 main stages:

- 1) appearance of nucleus of crystallization;
- 2) growth of crystals from the nucleus;
- 3) aggregation of crystals with the formation of polycrystalline precipitate.

These stages occur at different rates. That's why when $C(\text{Ag}^+) \cdot C(\text{Cl}^-) > K_s$ the precipitate of silver chloride is not always formed. The last stage can last for several hours or even days.

The following generalizations can be made regarding the relative values of K_s^0 and the reaction ion activities product:



1) If $a^m(\text{A}^{n+}) \cdot a^n(\text{B}^{m-}) < K_s^0$ the solution is unsaturated and there is no precipitation.

2) If $a^m(\text{A}^{n+}) \cdot a^n(\text{B}^{m-}) = K_s^0$ the solution is saturated and there is equilibrium.

3) If $a^m(\text{A}^{n+}) \cdot a^n(\text{B}^{m-}) > K_s^0$ precipitation will occur spontaneously until ion product equals the K_s^0 .

The dissolution of the precipitate or the equilibrium shift to the right can be carried out with the help of any method of the decrease of free cation (A^{n+}) or free anion (B^{m-}) concentration:

- 1) by binding of these ions into another less soluble precipitate;
- 2) by binding of metal ions into a complex;
- 3) by binding of anions into a slightly dissociated acid;
- 4) by oxidation or reduction of a cation or an anion.

COMPETITIVE EQUILIBRIA IN HETEROGENEOUS SYSTEMS

In real systems we can rarely find cases when only one heterogeneous equilibrium takes place. The presence of a great amount of ions in biological fluids leads to the simultaneous formation of several slightly soluble electrolytes.

When we consider competitive heterogeneous equilibria involving different types of electrolytes CaC_2O_4 (two ions) and $\text{Ca}_3(\text{PO}_4)_2$ (five ions), the calculations become more complicated.

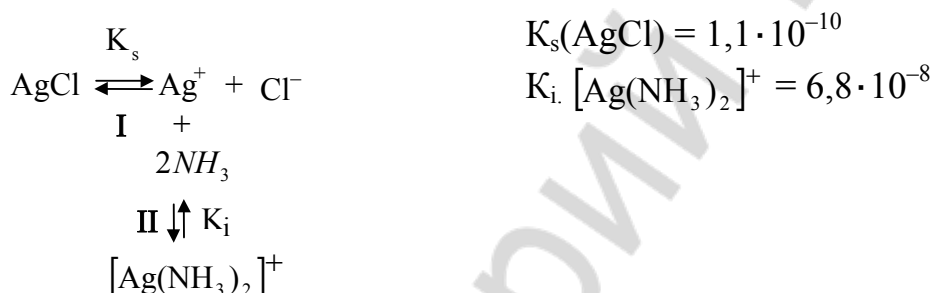
COMPETITIVE EQUILIBRIA OF DIFFERENT TYPES

Together with heterogeneous equilibria in real systems we can also find:

- equilibrium with the formation of complex compounds (binding of metal ions of a slightly soluble strong electrolyte into a complex);
- acid-base equilibrium (binding of anions of a slightly soluble strong electrolyte into a slightly dissociated acid);
- redox equilibrium (oxidation and reduction of ions of a slightly soluble strong electrolyte).

1. The influence of the equilibrium with the formation of a complex compound on heterogeneous equilibrium.

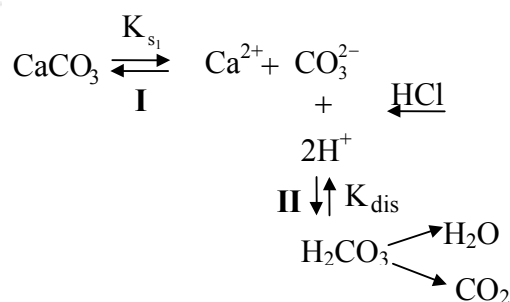
Let's consider a system of two different types of equilibrium.



When ammonia is passed through the saturated solution of silver chloride AgCl (heterogeneous equilibrium I) a complex ion $[\text{Ag}(\text{NH}_3)_2]^+$ is formed and a new equilibrium caused by the dissociation of this complex ion (homogeneous equilibrium II) occurs. In the result of the complex ion formation the activity of Ag^+ ions decreases and silver chloride AgCl begins to dissolve. While adding more ammonia we can dissolve AgCl precipitate completely. The more durable is the complex ion the more shifted is the equilibrium to the side of the complex ion formation and the dissolution of the precipitate.

2. The influence of acid-base equilibrium on heterogeneous equilibrium.

Let's consider the dissolution of calcium carbonate with the formation of slightly dissociated weak carbonic acid.

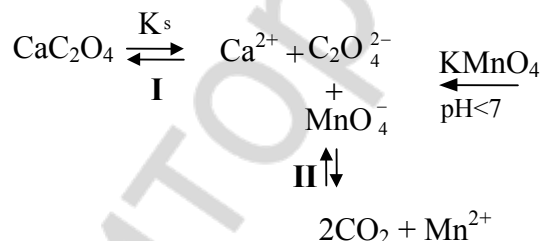


At first the solution contacting calcium carbonate precipitate CaCO_3 is saturated with respect to this precipitate. It means that the product of ion concentrations $C(\text{Ca}^{2+}) \cdot C(\text{CO}_3^{2-})$ equals the solubility constant of calcium carbonate $K_s(\text{CaCO}_3)$, (heterogeneous equilibrium I). When adding hydrochloric acid hydrogen ions begin binding carbonate ions CO_3^{2-} in the molecules of carbonic acid which then disintegrates into CO_2 and H_2O . The amount of carbonate ions decreases in the solution, i. e. a part of a precipitate converts into the solution. There is a new homogeneous equilibrium II. At the addition of a certain amount of an acid, i. e. at a certain pH value there is a complete dissolution of calcium carbonate precipitate.

In biological systems both in case of a norm and a pathology calcic salts are a solid phase and their solubility increases with the increase in acidity.

3. The influence of redox equilibrium on heterogeneous equilibrium.

The dissolution of the precipitate can happen in the result of a change in the oxidation number of an element which is a part of a solid phase, i. e. at redox processes. For the precipitate with the properties of a reducing agent we should choose rather a strong oxidizing agent and for the precipitate with the properties of an oxidizing agent we should choose a strong reducing agent. For example, anion $\text{C}_2\text{O}_4^{2-}$ of a slightly soluble electrolyte of calcium oxalate CaC_2O_4 is a reducer, the best oxidizer for which are the permanganate ions MnO_4^- added to the system in the form of potassium permanganate solution:



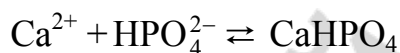
In both of these systems (I – heterogeneous, II – homogeneous) there is the competition to get the oxalate-ion $\text{C}_2\text{O}_4^{2-}$. The permanganate ion MnO_4^- which oxidizes the oxalate-ion and the precipitate is finally dissolved and the emission of CO_2 quickly shifts the equilibrium to the side of the dissolution of precipitate.

For the precipitate to be dissolved we should choose the reducing or oxidizing agent according to the value of their redox potentials. For example, for the precipitate with the properties of a reducing agent we should choose rather a strong oxidizing agent and for the precipitate with the properties of an oxidizing agent we should choose a strong reducing agent. For example, to dissolve CaC_2O_4 we'd better take KMnO_4 than I_2 , because $\varphi^0 \text{H}_2\text{C}_2\text{O}_4/2\text{CO}_2 = -0,49\text{V}$; $\varphi^0 \text{MnO}_4^-/\text{Mn}^{2+} = +1,51\text{V}$; $\varphi^0 \text{I}_2/2\text{I}^- = +0,5\text{V}$. In the first case $\Delta\varphi^0 = +1,51 - (-0,49) = 2,0\text{V}$ and in the second $\Delta\varphi^0 = +0,5 - (-0,49) = 0,99\text{V}$, i. e. twice less.

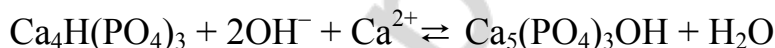
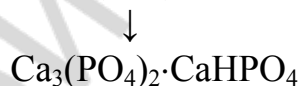
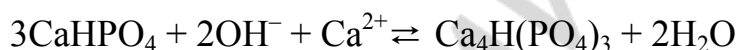
HETEROGENEOUS EQUILIBRIA IN THE VITAL ACTIVITY OF AN ORGANISM

In a human body the formation of bone tissue is the most important heterogeneous process with inorganic substances participating in it. The main mineral component of bone tissue is calcium hydroxide phosphate $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Part of Ca^{2+} ions is substituted by Mg^{2+} ions and a very negligible amount of OH^- ions is substituted by fluorine ions which increase the durability of bones.

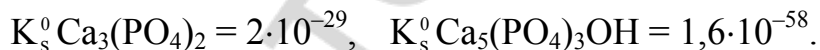
The formation of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ from weak alkali solutions «in vitro» experiments can be explained in the following way. At physiological value of blood pH (7,4) ions HPO_4^{2-} and H_2PO_4^- are known to coexist in the system. The comparison of values of solubility constants $K_s^0(\text{CaHPO}_4) = 2,7 \cdot 10^{-7}$ and $K_s^0\text{Ca}(\text{H}_2\text{PO}_4)_2 = 1 \cdot 10^{-3}$ indicates that the precipitate CaHPO_4 is firstly formed in the presence of Ca^{2+} ions.



Then the formed compound undergoes the following changes:



The solubility in the row $\text{CaHPO}_4 \rightarrow \text{Ca}_4\text{H}(\text{PO}_4)_3 \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH}$ constantly decreases, which helps to form the last compound:



It goes without saying that the processes of calcium phosphate precipitation which are the basis for the bone tissue formation are much more complex.

Blood plasma is an almost saturated solution of calcium hydrophosphate phosphate CaHPO_4 which is in dynamic equilibrium with inorganic constituent parts of bone tissue. If the product of ion Ca^{2+} and HPO_4^{2-} concentrations is increased in the blood, there is the calcification and if it decreases, the content of inorganic components in bones is decreased too.

When the Ca^{2+} ion concentration in blood plasma is increased we can observe the equilibrium shift which leads to calcium deposition in bone tissue. And on the contrary, the decrease in Ca^{2+} ion concentration in blood plasma also causes the equilibrium shift but now accompanied by the dissolution of mineral components of bone tissue. For example, in the case of rickets when there is insufficient adsorption of Ca^{2+} ions from the gastrointestinal tract their concentration in blood plasma remains constant due to the release of Ca^{2+} ions from the inorganic components of bones.

Due to such a phenomenon as isomorphism together with calcium salts there is also the precipitation of cations of other salts like beryllium, strontium and barium salts similar to calcium ions in their properties.

The presence of even small amounts of beryllium in the environment leads to such a disease called berylliosis (beryllium rickets). The thing is that Be^{2+} ions displace Ca^{2+} ions from bone tissue causing osteomalacia.

Strontium ions form insoluble compounds with the same anions as calcium ions. Part of strontium ions Sr^{2+} is also a part of bone tissue. The excess of strontium ions causes bone fragility (strontium rickets). But of the greatest danger can be radioactive nuclide strontium-90 (period of half-decay is 27,7 years, pure β -emitter). Its sources can be radioactive dust, drinking water, vegetal and diary products. Settling in bones, Sr^{90} irradiates the marrow and breaks hematosis.

Calcium ions Ca^{2+} together with oxalate ions can form depositions of calcium oxalate or so called oxalate calculus. It is formed in kidneys, bladder, and are the reason of urolithiasis. Besides calcium oxalate, calcium phosphate and calcium urate are also part of calculus.

The main principle in treatment of urolithiasis is the calcium extraction from concrements with its further transfer into the form of soluble compounds. The most widely used method of such extraction is the influence on the calculus by some complex formers interacting with ions of bivalent metals which are part of the calculus (chelation therapy). These can be ethylenediaminetetraacetic acid and its salts, citric acid and its salts.

CONTENTS

Preface	3
Chapter I. The Electron Shell of the Atom. Electron Configurations of Elements. The Periodic Table. Atomic Properties and Periodic Trends	4
Chapter II. Chemical Bond.....	17
Chapter III. Complex (coordination) compounds	33
Chapter IV. Heterogeneous equilibria.....	39