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КАФЕДРА ОБЩЕЙ ХИМИИ

**ОСНОВЫ ХИМИИ ДЛЯ ИНОСТРАННЫХ
СТУДЕНТОВ**

**ESSENTIAL CHEMISTRY FOR FOREIGN
STUDENTS**

Учебно-методическое пособие



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PREFACE

Our goal in writing of this guide to present the material that is essential for a one-year foreign student. This guide is based on the lectures on General, Biophysical and Colloidal chemistry which are being delivered in the Byelorussian state medical university.

We have made an effort to write only those concepts which are either useful in the General, Organic and Biological chemistry or which help to give a picture of what presently concerns the future doctor.

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.

Chemical thermodynamics and kinetics are fundamental to many disciplines other than chemistry. For example the most general problems of chemical thermodynamics are necessary for understanding of energy characteristics of chemical and physico-chemical processes of vital activity of organism. On the other hand the problems of chemical kinetics are necessary for pharmacokinetics and toxicology. These facts predisposed the laconic character of writing and led to inevitable simplification of the material given in chapter three and chapter four.

The chapter five describes the process of solution formation and thermodynamics of dissolving and shows that the dissolving is a spontaneous process. The concept of the ideal and non-ideal solutions is discussed. In this chapter we assess the colligative properties of solutions, paying special attention to their significance in medicine and pharmacology. We investigate the solution electrolytic behaviours in general.

The principles of dynamic acid-base equilibrium and the action mechanism of buffer solutions are given in chapter six.

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 seven 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 eight describes the theory of heterogeneous equilibria and explains their biochemical influence on the formation on bone tissue in a human body.

The chapter nine is a general introduction to electrical conduction of tissues and biological fluids. The application of conductometry in medical biological research is described. Concept about the electrode and oxidation-reduction potentials is given.

The chapter ten includes the physico-chemistry of surface phenomena. In this chapter we examine surface energy and surface tension, surface active and surface inactive substances, concentrating mainly on the meaning of these properties in medicine.

The principles of chromatography are given in chapter eleven. Practical application of different types of chromatography in biology and medicine is described.

Certain phenomena connected with the colloidal state of matter are given in chapter twelve.

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 1

BASIC CONCEPTS ABOUT THE STRUCTURE OF MATTER

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 1.1

Table 1.1

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).

1.1. The electron shell of the atom

Energy levels. 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.,

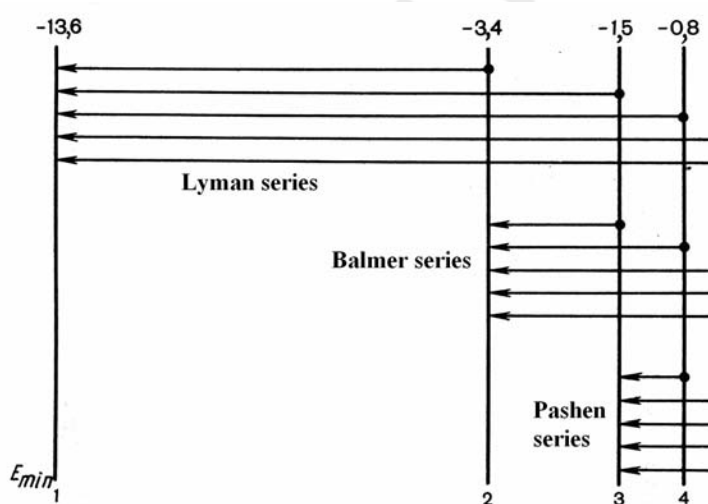


Fig. 1.1. Diagram of the energy levels and quantum transitions of the electron of a hydrogen atom

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 in passing 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 (fig. 1.1). The Bohr's theory established the basis for

quantum mechanics. It studies motion laws that govern the behavior of small particles.

The wave nature of microparticles motion. Before all of the experiments mentioned above, 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 (ν) has a certain wavelength (λ):

$$\lambda = h / m \nu,$$

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.

The uncertainty principle. In 1927, Werner Heisenberg set for the first time the uncertainty principle according to which it is impossible to determine accurately both the position (or coordinates) and the velocity of motion of a microparticle simultaneously. The mathematical expression of the uncertainty principle is:

$$\Delta x \cdot \Delta \nu > h/2\pi m$$

where Δx , $\Delta \nu$ 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.

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 moment of

time in the three-dimensional space around the nucleus. The position of an electron is shown on the photographs as a dot (fig. 1.2). 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 fig.1.3.

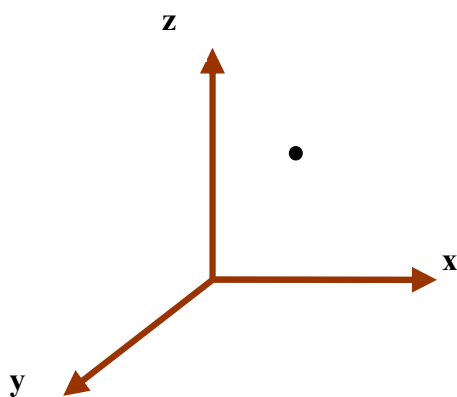


Fig. 1.2. The position of an electron

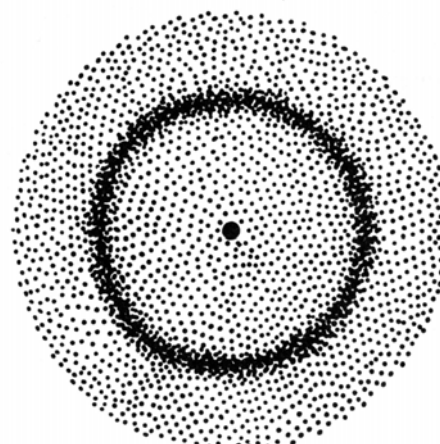


Fig. 1.3. A possible form of the electron cloud in an atom

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. The configuration and size of the electron cloud is usually regarded as the shape and size of the orbital.

1.2. The quantum numbers

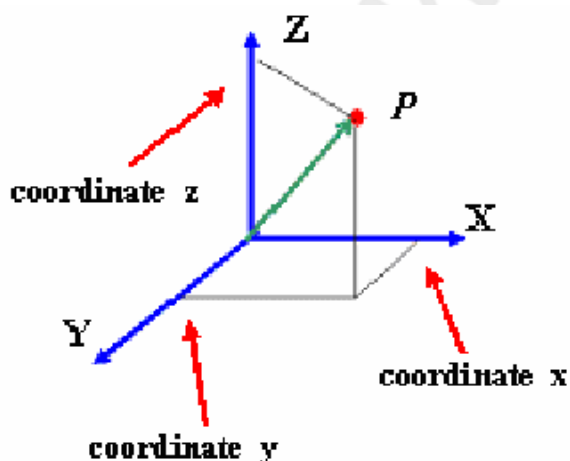


Fig. 1.4. The Cartesian coordinate system. The position of a point P in space can be specified by giving the x, y and z coordinates

In a three-dimensional world, three parameters are required to describe the location of an object in space (fig. 1.4). 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 1.2).

Table 1.2

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 .

In approximately 1920, theoretical chemists realized that, since electrons interact with a magnetic field, there must be one more concept to explain the behaviour 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 (fig. 1.5); that is, the electron acts like a tiny bar magnet.

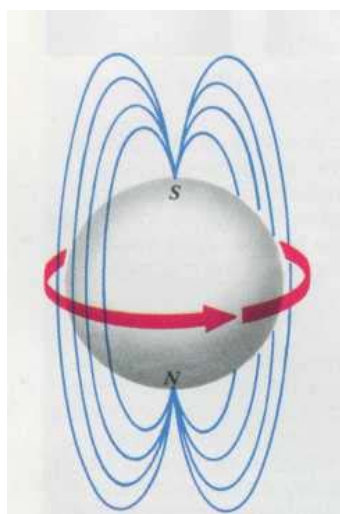


Fig. 1.5. Electron spin

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.

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

All s orbitals are spherical in shape, but the 2s cloud is larger than the 1s cloud (fig. 1.6.): the point of maximum probability for the 2s electron is found slightly farther from the nucleus than that of the 1s electron.

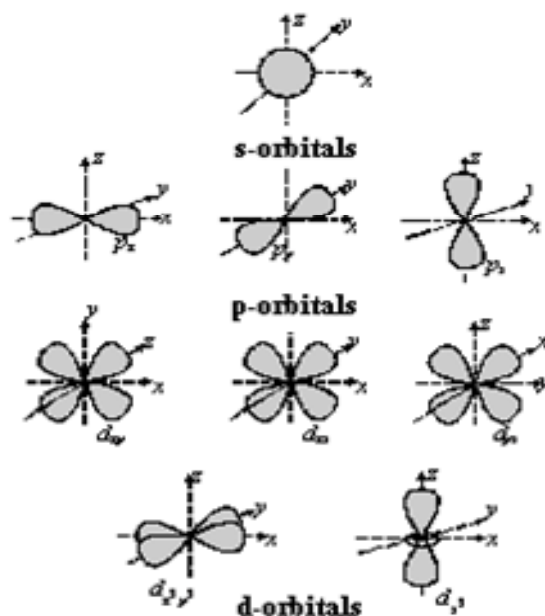


Fig. 1.6. The shapes of atomic orbitals

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

According to table 1.2, 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).

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.

1.3. Electron configurations of elements

The Pauly 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 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

$$n = 1, \ell = 0, m_\ell = 0, m_s = +1/2$$

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

$$n = 1, \ell = 0, m_\ell = 0, m_s = -1/2$$

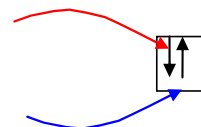
The pictures above are appropriate for the H atom in its ground state: one electron in the 1s orbital.

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 $n = 1$, $\ell = 0$, $m_\ell = 0$, $m_s = +1/2$



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 fig. 1.7.

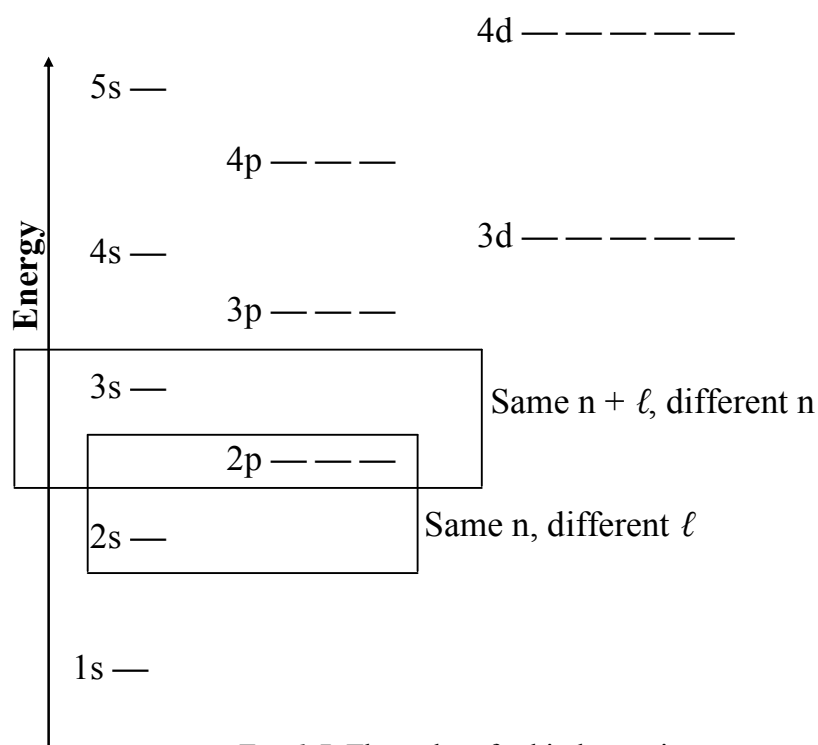


Fig. 1.7. The order of orbital energies

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 fig. 1.7, 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 $3d < 4s$ (fig. 1.7).

Electron configurations of the main group elements. Configurations of the first ten elements are illustrated in table 1.3. 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 fig. 1.8, 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».

Table 1.3

Electron Configurations of the Elements with $Z = 1$ to 10

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

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 $ns^2 np^x$ where $x =$ group number.

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.

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 1.4 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 1.4

Orbital Box Diagrams for the Elements Ca Through Zn

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

1.4. The periodic table. Atomic properties and periodic trends

Atomic size. For the main group elements, atomic radii increase going down a group in the periodic table and decrease going across a period (fig. 1.8).

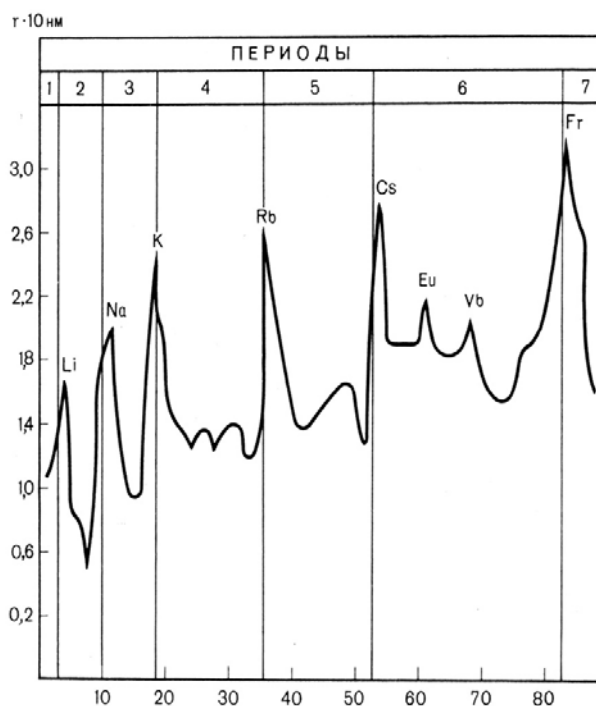


Fig. 1.8. Atomic radii of the elements

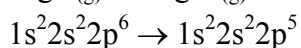
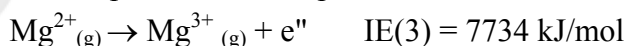
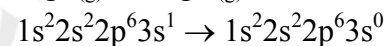
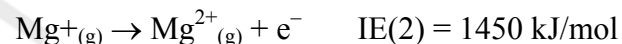
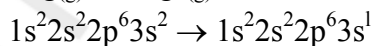
The reason atomic radii increase on descending a periodic group is clear. Going down Group 1A, for example, the last electron added is always assigned to an s orbital and is in the electron shell beyond that used by the electrons of the elements in the previous period. The inner electrons shield or screen 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.

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

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 $(g) + \text{energy} \rightarrow \text{Atom}^+(g) + e^-$, $\Delta E = \text{ionization energy (IE)}$

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 $\text{Mg}_{(g)}$ 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 in-

creases 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 (fig. 1.9), 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.

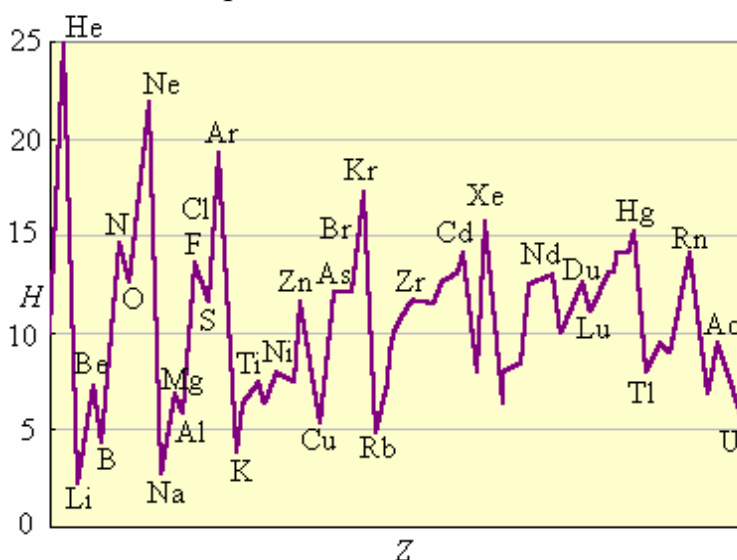


Fig. 1.9. First ionization energies of the elements

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 1.5.

Table 1.5

Electron Affinities for the first and the second period elements

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

$\text{F}_{(g)} + e^{-} \rightarrow \text{F}^{-}_{(g)} + 322 \text{ kJ/mol}$. 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: $\text{N}_{(g)} + e^- \rightarrow \text{N}^-_{(g)}$, 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 2 CHEMICAL BOND

2.1. 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 behaviour 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	$1s^2 2s^2 2p^6$	$3s^1$	1A
Si	$1s^2 2s^2 2p^6$	$3s^2 3p^2$	4A
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6$	$4s^2 3d^2$	4B
As	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	$4s^2 4p^3$	5A

From the table above you see that the number of valence electrons of each element 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 behaviour 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.

2.2. 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 fig. 2.1 sodium initially has one valence electron, and chlorine has seven.

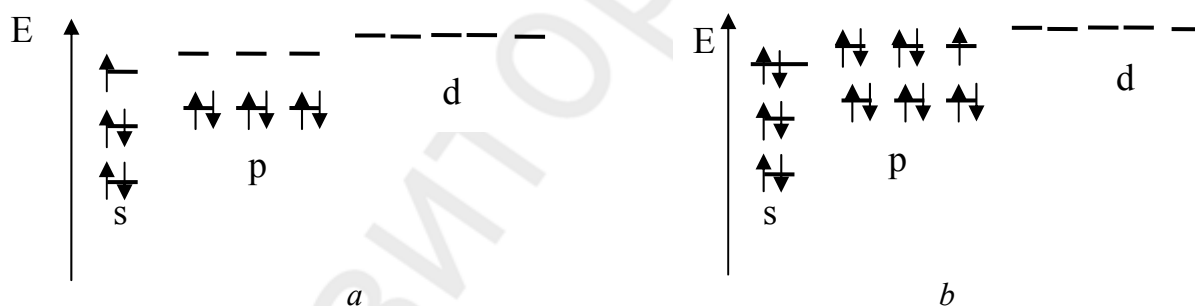
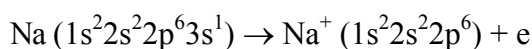


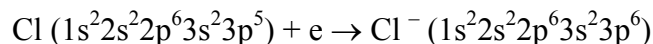
Fig. 2.1. Formation of an ionic bond:
a — sodium atom, *b* — chlorine atom

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:

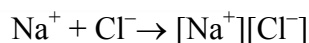
Step1. Sodium loses its outer electron and becomes positively charged



Step2. 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).

2.3. 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 (fig. 2.2).

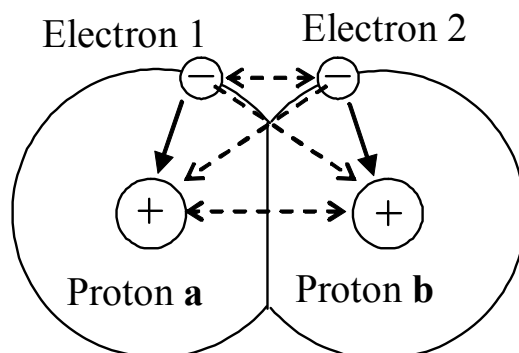


Fig. 2.2. The formation of a covalent bond in H_2 molecule. Pair of electrons (one electron from each atom) flows into the internuclear region and is attracted to both nuclei. It is this mutual attraction of 2 (or sometimes 4 or 6) electrons by two nuclei that leads to a force of attraction between two 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 fig. 2.3 shows the energy changes as a pair of electrons initially associated with separate H atoms becomes a bonding pair in H₂. 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.

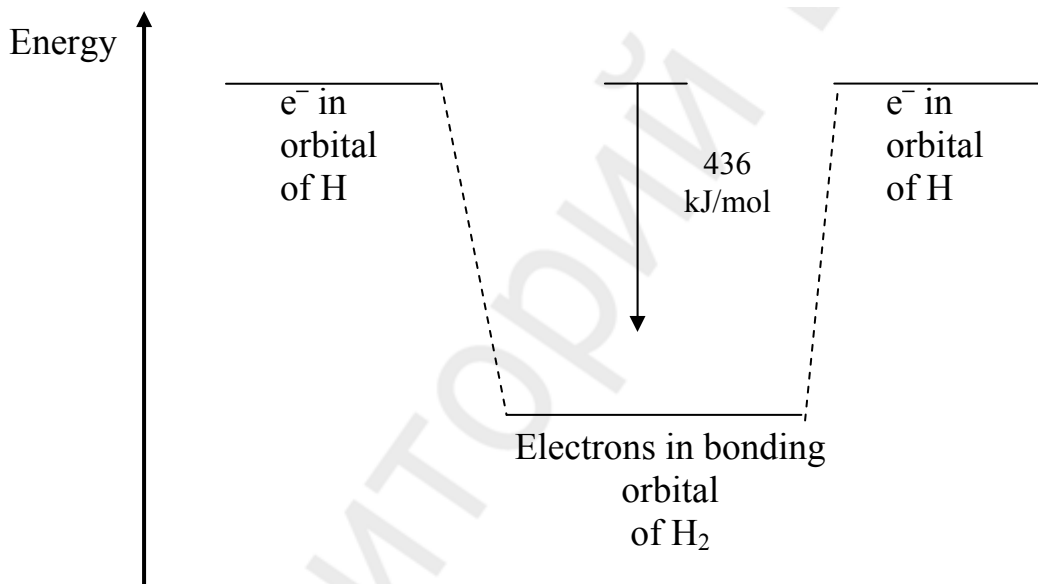


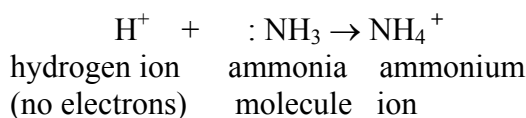
Fig. 2.3. Energy changes occurring in the process of bond formation between two H atoms

2.4. Properties of Covalent Bond

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 H₂C=CH₂, N \equiv 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.

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.

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.

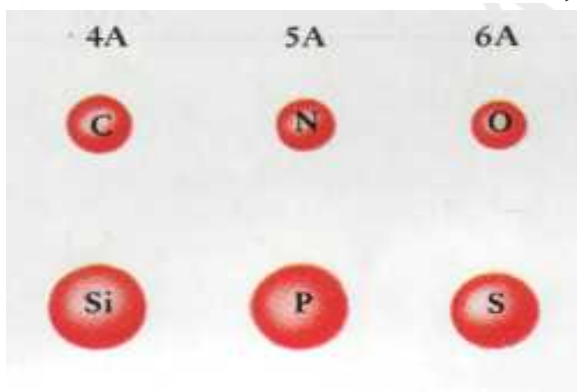


BOND ORDER = 2. The order is 2 when there are two shared pairs between two atoms. One of these pairs forms a sigma bond and the other pair forms a pi bond. Examples are the C=O bonds in CO₂ and the C=C bond in ethylene, C₂H₄.

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⁻).



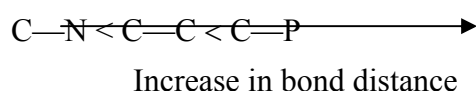
Bond length. The most important factor determining **bond length**, the distance between two bonded atoms, is the sizes of the atoms themselves. For



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 (fig. 2.4).

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

Fig. 2.4. Relative Atom Sizes for Groups 4A, 5A, and 6A.



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.

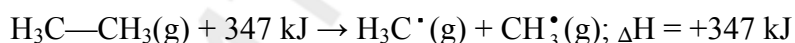
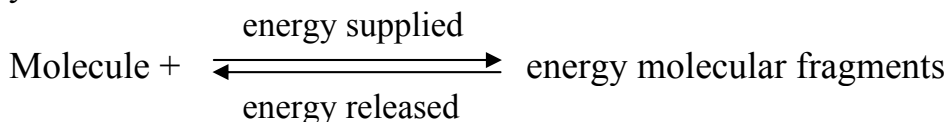
The effect of bond order is evident when you compare bonds between the same two atoms. For example, the bonds become shorter as the bond order increases in the series C—O, C=O, and C≡O.

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

Adding a π 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 π bond results in a 9 pm reduction in bond length from C=O to C≡O.

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 ($\text{H}_3\text{C—CH}_3$), ethylene ($\text{H}_2\text{C=CH}_2$), and acetylene ($\text{HC}\equiv\text{CH}$) 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.

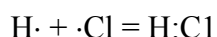


The energy that must be supplied to a gaseous molecule to separate two of its atoms is called the *bond dissociation energy* (or *bond energy* for short) and is given the symbol E_b . As E_b represents energy supplied to the molecule from its surroundings, E_b has a positive value, and the process of 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 $\text{H}_3\text{C—CH}_3$ from two $\text{CH}_3^\cdot(\text{g})$ fragments is -347 kJ/mol .

Polarity and electronegativity. Oxidation numbers. Covalent bonds are classified as polar or nonpolar. For example, the bonds in H_2 and Cl_2 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 we can presume that the bond pair is shared equally between the two atoms.

In H_2 and Cl_2 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 H_2 and Cl_2 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:



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.

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 below. Although you do not yet know how to predict the structures 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
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 (fig. 2.5).

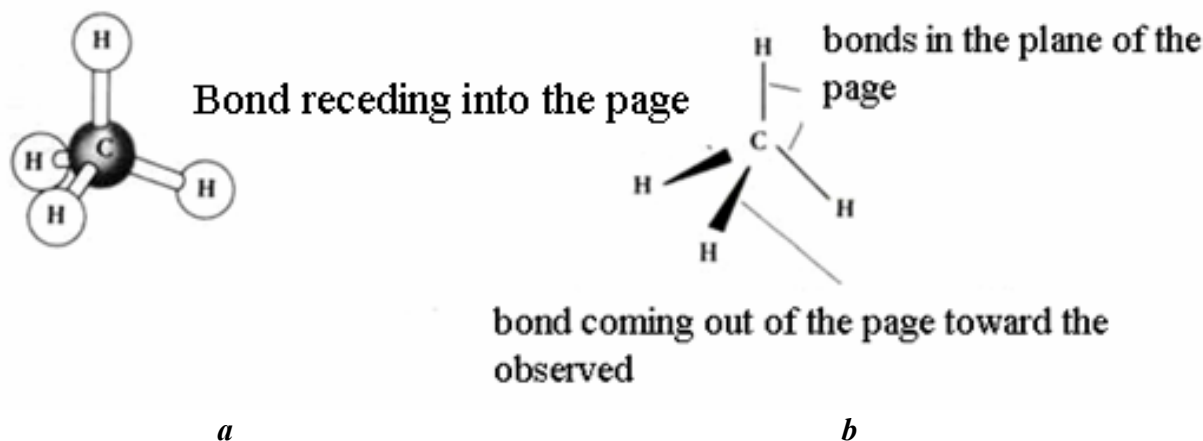


Fig. 2.5. The structure of methane, CH_4 , to show the ways molecular structures will be illustrated:


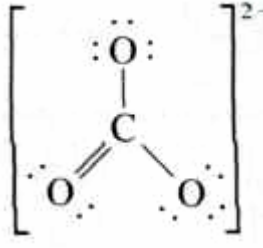
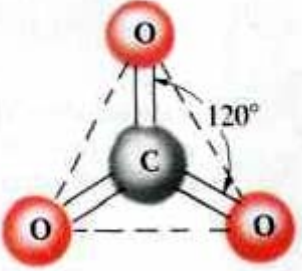
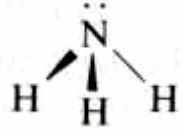
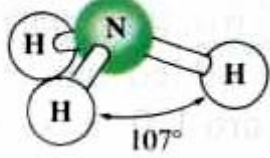
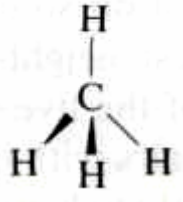
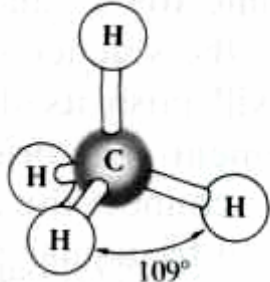
a — drawing of a ball-and-stick model, *b* — perspective drawing.

The adjective «polar» was used 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

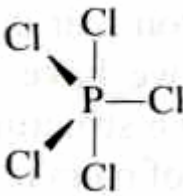
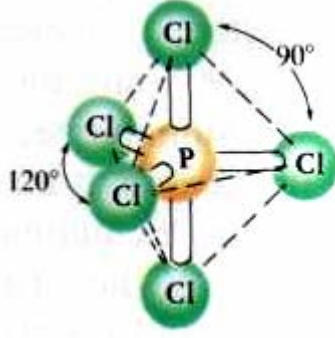

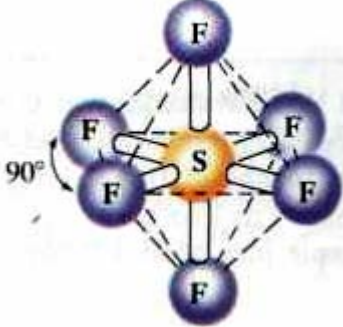
that one end of the molecule bears a slight negative charge, δ^- ; the other end has a slight positive charge of equal value, δ^+ . The experimental measure of this separation of charge is the molecule's dipole moment, which is defined as the product of the size of the charge (δ) and the distance of separation. The units of dipole moment are therefore coulomb \cdot 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 2.1

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		

End table 2.1

PCl ₅	Trigonal bipyramidal		
SF ₄	Octahedral		

2.5. 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.

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 (fig. 2.6). If two H atoms approach each other closely enough, their 1s orbitals can partially occupy the same region of space.

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.

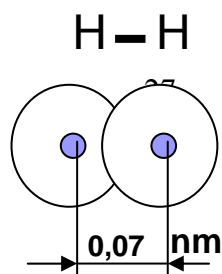


Fig. 2.6. The orbital overlap between the two H atoms

As the extent of overlap between two orbitals increases, the strength of the bond increases. This is seen in fig. 2.7 as a drop in energy as two H atoms, originally far apart, come closer and closer together.

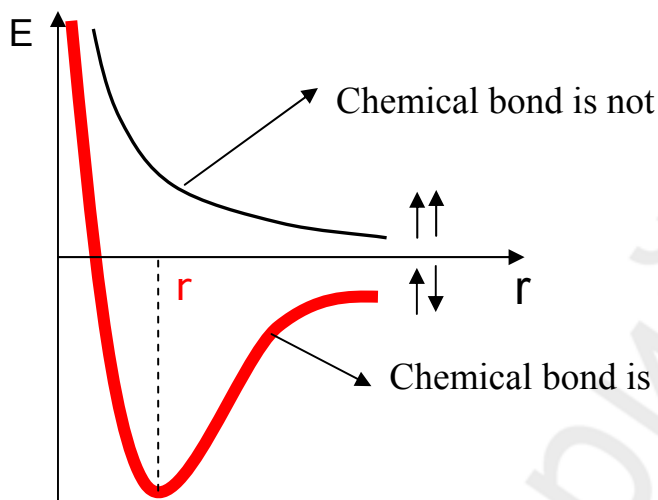


Fig. 2.7. Total potential energy change in the course of H-H bond formation

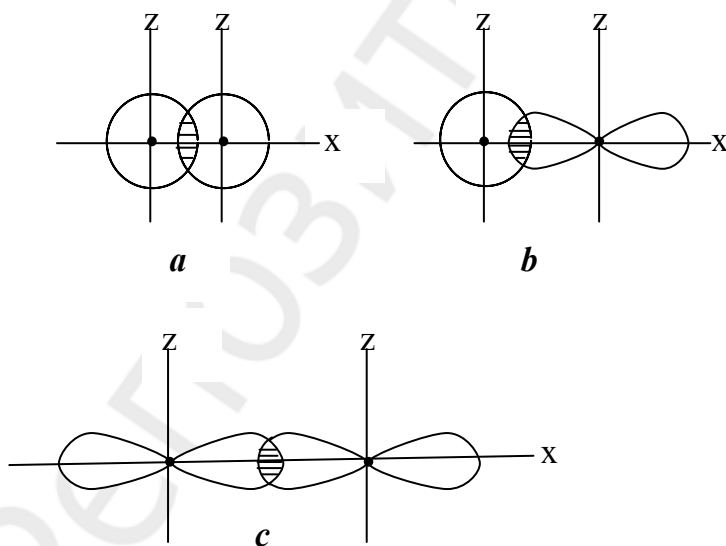


Fig. 2.8. The formation of σ -bond:

$a - s - s$; $b - s - p$; $c - p_x - p_x$

H
another, the energy increases rapidly, due to the repulsion of the positive nu-
ose to one
positive nu-

cleus 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.

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 (fig. 2.8.). 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.

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 2.1).

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 (fig. 2.9). Each hybrid orbital combines the properties of its *s* and *p* orbital parents.

The theory of orbital hybridization is an attempt to explain how in CH₄ 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 CH₄, for instance, and stronger bonds result than without hybridized orbitals.

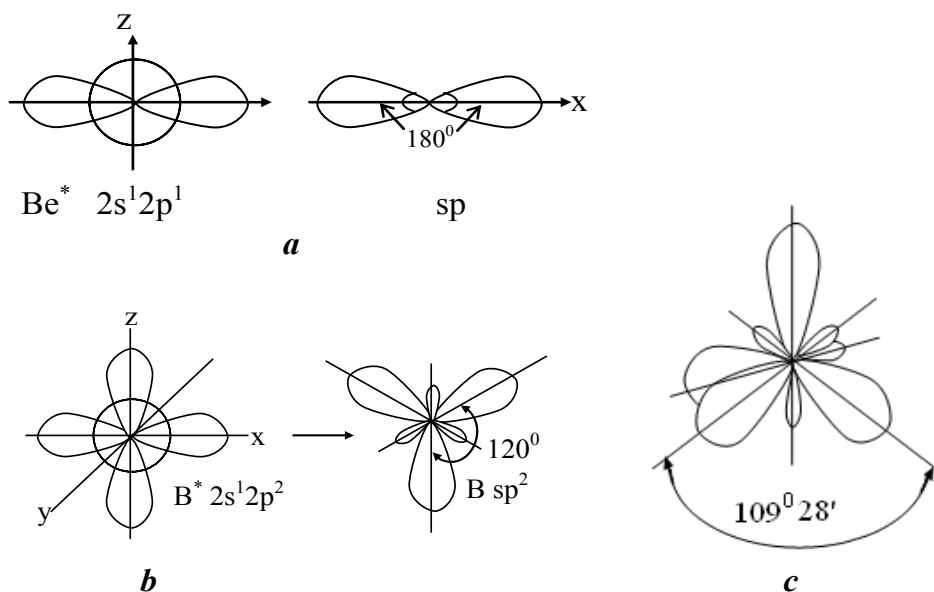
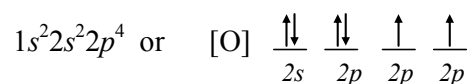


Fig. 2.9. Types of orbital hybridization:
a — sp — hybridization; *b* — sp^2 — hybridization; *c* — sp^3 — hybridization

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 (fig. 2.10). 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.

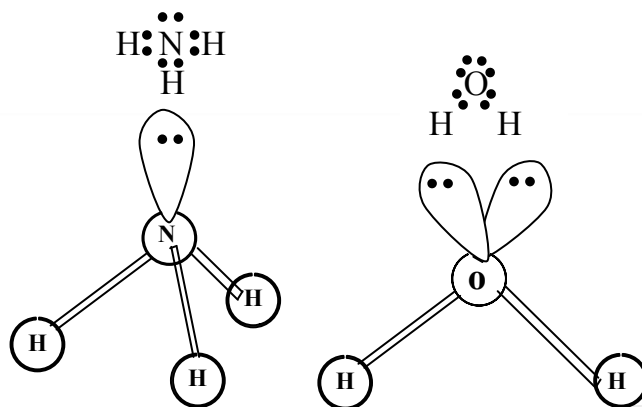


Fig. 2.10. Orbital hybridization in H₂O and NH₃ molecules

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 O₂ 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 O₂ molecule is *paramagnetic* and that it has exactly two unpaired electrons per molecule. It is sufficiently magnetic that solid O₂ clings to the poles of a magnet. The molecular orbital approach can account for the paramagnetism of O₂ more easily than the valence bond theory. To see how MO theory can be applied to O₂ 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 H₂ molecule.

Bonding and antibonding molecular orbitals in H₂. 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 (fig. 2.11). The average energy of the molecular orbitals is slightly higher than the average energy of the parent atomic orbitals.

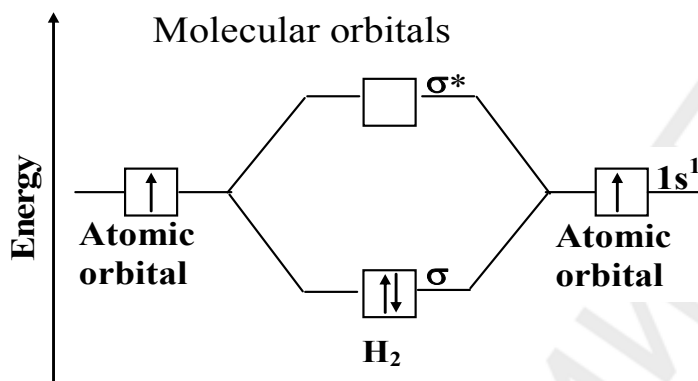


Fig. 2.11. Bonding and antibonding molecular orbitals in H₂

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 H₂ is lower than that of either parent 1s electron, the H₂ molecule is stable. We write the electron configuration H₂ as $(\sigma_{1s})^2$.

Next consider putting two helium atoms together to form He₂. Since both He atoms have 1s valence orbitals, they combine to produce the same kind of molecular orbitals as in H₂. The four helium electrons are assigned to these orbitals according to the scheme shown in fig. 2.12.

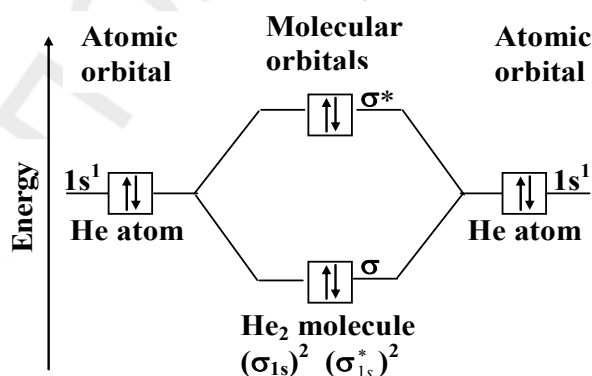


Fig. 2.12. Energy level diagram for the hypothetical He₂ molecule

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.

Bond order. Bond order = number of electron pairs in bonding molecular orbitals — number of electron pairs in antibonding molecular orbitals.

In the H_2 molecule, there is one electron pair in a bonding orbital, so H_2 has bond order of 1. In contrast, the effect of the σ_{1s} pair in He_2 is canceled by the effect of the σ_{1s}^* pair, so the bond order is 0. Fractional bond orders are also possible. For example, even though He_2 does not exist, the He_2^+ ion has been detected. Its molecular orbital electron configuration would be $(\sigma_{1s})^2(\sigma_{1s}^*)^1$. Here there is one electron pair in a bonding molecular orbital, but one-half part in an antibonding orbital. Therefore, the net bond order is $\frac{1}{2}$.

Electron configurations for homonuclear, diatomic molecules. Molecular orbital electron configurations are given for the diatomic molecules B_2 through F_2 in table 2.2. We find there is an excellent correlation between the electron configurations and the bond orders, bond lengths, and bond dissociation energies shown at the bottom of the table.

Table 2.2

Molecular Orbital Occupations and Physical Data for Homonuclear, Diatomic Molecules of Second Period Elements

	B_2	C_2	N_2	O_2	F_2
σ_{2p}^*	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
π_{2p}^*	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>
σ_{2p}	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
π_{2p}	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/>
$\sigma_{2x}^* \text{S}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
$\sigma_{2x} \text{S}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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

B_2 and C_2 are not ordinary molecules; C_2 , for example, has been observed only in the vapor phase over solid carbon at high temperatures. It is, however, worth noticing that the higher predicted bond order for C_2 than for

B_2 agrees well with the higher bond dissociation energy and shorter bond length of C_2 .

We know from experiment (and have also predicted from the electron dot structure) that N_2 is a diamagnetic molecule with a short, strong triple bond. The molecular orbital picture is certainly in agreement, predicting a bond order of 3.

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 2.2.

CHAPTER 3 CHEMICAL THERMODYNAMICS

In the living organisms, the chemical energy is transformed to other forms of energy. Bioenergetics studies the transformation of different kinds of energy in the living organisms. Chemical thermodynamics is the base of bioenergetics.

Thermodynamics is the science about mutual conversions of different kinds of energy and transmission of energy in the form of heat and work .

There are three problems of chemical thermodynamics

1.Determination of the energy effects of the chemical and physico-chemical processes.

2.Determination of the possibility, direction and limits of spontaneous processes under given conditions.

3.Determination of the conditions of equilibrium of the systems.

3.1. Terminology of chemical thermodynamics

It is necessary to define precisely certain concepts, terms and quantities used in thermodynamics since any *ambiguity* can lead to wrong conclusions.

A thermodynamic system is a body or group of interacting bodies which we consider apart from its surroundings .For example, a gas in a vessel, a cell ,a plant, an organ, etc .

The following thermodynamic systems are known according to the character of interactions of its surroundings.

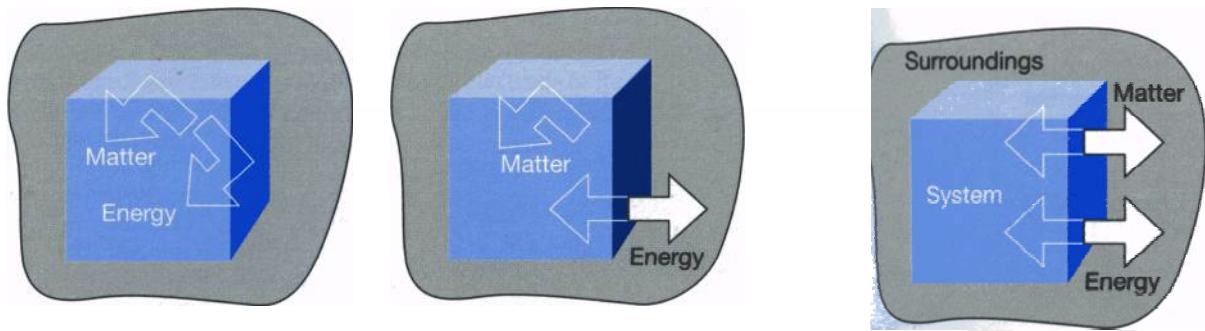


Fig. 3.1. Thermodynamic systems

1. An *isolated system* is one which cannot exchange energy or matter with its surroundings. There are no such systems in the nature.

2. A *closed system* is one which can exchange energy but not a matter with its surroundings. For example an electric lamp.

3. An *opened system* is one which can change energy and matter with its surroundings. For example, a living organism.

A *homogeneous system* is one consisting of a single phase, no any boundary surfaces, all parts of the system have the same physical and chemical properties. For example, the mixture of gases, the solutions.

A *heterogeneous system* is one consisting of several phases, has boundary surfaces and different physical and chemical properties. For example, an ice is in water, liquid and vapour.

A *phase* is the part of the system with the same physical and chemical properties. For example, ice-water (an ice is the first phase, water is the second phase).

The thermodynamic quantities of the state of the system. The thermodynamic quantities characterize the state of the system. The *independent thermodynamic quantities* can be measured. They are: temperature, pressure, mass, volume and density.

Thermodynamic quantities whose value depends only on the state of the system are called *functions of state*. The change of such quantities in a process depends only on the initial and final states of the system, it doesn't depend on the path by which the system is brought from one state to the other. For example, the internal energy depends on temperature, concentration, etc. It is impossible to determine the absolute value of functions of state, because they depend on the other thermodynamic quantities.

The functions of state are: U—the internal energy;

H—the enthalpy;

S—the entropy;

G—the Gibb's free energy.

Thermodynamic processes. Any change in the state of system is the thermodynamic process. Two types of thermodynamic processes are distinguished.

A *reversible thermodynamic process* is defined as a process in which the system *reverts* to its initial state without having caused any changes in its surroundings. If changes do take place in the surroundings, then the process is *irreversible*.

It must be stressed that reversibility and irreversibility, as defined in thermodynamics, do not coincide with the concepts, as applied to chemical reactions in chemistry, where the term «reversible» frequently denotes that a reaction may proceed in either direction, although the return to the initial state leads to changes in the surroundings.

Processes which are carried out at constant temperature are called *isothermal*. ($T = \text{const}$, $\Delta T = 0$)

If a reaction proceeds at constant volume ($V = \text{const}$, $\Delta V = 0$), the process is *isochoric*. Chemical reactions proceed more frequently at constant pressure. The process is *isobaric* ($p = \text{const}$, $\Delta p = 0$).

Adiabatic processes are those in which the system neither absorbs nor gives up heat on its surroundings.

3.2. Energy. Internal energy

The quantitative measure of motion of matter is energy. Energy can exist in various forms, all of which are forms of motion of matter. The forms of motion of matter are various and therefore the forms of energy are various as well (mechanical, electric, chemical, etc.) Every form of motion of matter corresponds to its form of energy. The various forms of energy transform into each other. For example, transformation of chemical energy into other forms of energy in a living organism (mechanical, heat energy, electric, etc.).

The joule (J) is a unit of energy. $1\text{J}=1\text{Nm}$ (Newton-meter). One calorie is equivalent to 4.184 joules.

The internal energy. One of the most important quantities in chemical thermodynamics is the internal energy U of the system. This quantity is a function of state.

The internal energy U of a substance (or system) is the total energy of the particles forming the substance. It consists of the kinetic and potential energies of the particles. The kinetic energy is the energy of translational, vibrational and rotational motion of the particles (atoms, molecules, ions, electrons); the potential energy is due to the forces of attraction and repulsion acting between the particles (intra-and intermolecular interactions):

$$U = E_{\text{kin}} + E_{\text{pot}}$$

The internal energy does not include the kinetic energy of motion of the system as a whole or its potential energy due to position. It is impossible at pre-

sent to determine the absolute value of the internal energy of a system, but changes in internal energy can be determined for various processes, and this is enough for the fruitful application of this concept in thermodynamics:

$$\Delta U = U_2 - U_1,$$

where U_1 and U_2 are the internal energy of the system in the initial (1) and the final (2) state, respectively. The quantity ΔU is considered positive if the internal energy of the system increases as a result of the given process.

The internal energy only depends on the initial and final states of the system; it does not depend on the path by which the system is brought from one state to the other. The internal energy obviously depends both on the amount of the substance and on the environmental conditions. As all other things being the same, the internal energy is directly proportional to the amount of substance.

Energy can be transferred from one part of a system to another in the form of heat or work or simultaneously. *Heat and work are not functions of state, they are forms of energy transfer.*

1. *The heat (Q) is the form of energy transfer which is carried out as disordered motion of matter under the temperature's gradient.*

Such form of energy transfer occurs by the temperature's gradient only. If T_1 is greater than T_2 ($T_1 > T_2$) the energy transfer will take place. The process stops when T_1 equals T_2 (i.e. $T_1 = T_2$).

How does the energy transfer? Look at fig. 3.2.

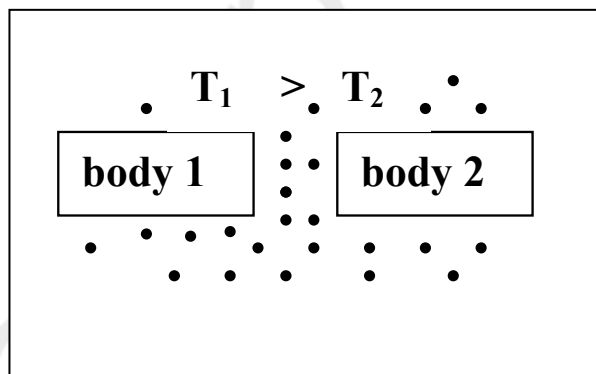


Fig. 3.2. The molecules move disorderly, collide with body 1, gain an excess of energy and then give to another molecules and at last to body 2

2. *Work* is one of the ways of transferring energy from one system (which performs work) to another system (on which work is performed). In the process the internal energy of the first system decreases, while that of the second system increases by an amount corresponding to the work performed (provided no heat has been transferred at the same time) fig.3.3.

The work (A) is the form of energy transfer which is carried out as ordered motion of matter. The work is connected with overcoming the force of friction and the movement of bodies in space.

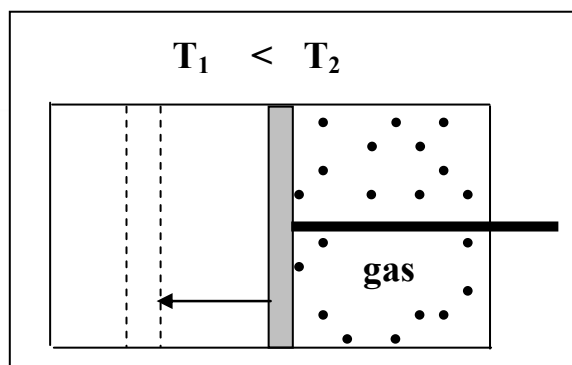


Fig. 3.3. The expansion of a gas makes piston to move

3.3. The first law of thermodynamics

The first law of thermodynamics is intimately related to the law of conservation of energy, which establishes the equivalence of the different forms of energy and the relation between the amount of heat absorbed or evolved in a process, the work performed or obtained, and the change in the internal energy of the system.

A number of consequences of this law are of great importance for physical chemistry and for the solution of various technological problems. By means of this law we can perform calculations of the energy balance, and in particular, the heat balance, and the heats of various processes. The first law of thermodynamics is a postulate; it cannot be proven by logical *reasoning*, but follows from the sum total of human experience. Its validity is demonstrated by the complete agreement of all its consequences with experience.

A great part in the formulation of the first law, as we know it today, was played by Hess, Joule and Meyer, Helm Holts and others.

The first law can be formulated in several ways, which are essentially equivalent to one another. One of its forms is as follows.

The heat energy (Q) flowing into a system can be used to change the internal energy of the system (ΔU) and allow the system to perform work (A) on its surroundings. This statement can be written in equation form as $Q = \Delta U + A$, where A is the work of expansion.

The following highly useful formulation of the first law is a direct consequence of the proposition that the internal energy of an isolated system is constant «*in any process the change in the internal energy of a system $\Delta U = U_2 - U_1$ is equal to the heat Q absorbed by the system minus the work A done by the system*»:

$$\Delta U = Q - A$$

It goes without saying, that all the quantities are to be expressed in the same units. This equation is the mathematical expression of the first law of thermodynamics. By means of it we can define the concept of internal energy thermodynamically as a quantity, the increase in which during a process is equal to the heat absorbed by the system plus the work done on the system by external forces.

The application of the first law of thermodynamics to various processes:

1. *An isochoric process.*

In the course of chemical reactions, work is mainly done against the force of the external pressure. This work depends on the change in the volume of a system. For an isochoric process $V = \text{const}$, $\Delta V = 0$, we have $A = 0$, $A = p\Delta V$, $Q_v = \Delta U + A$ and consequently *the mathematical expression for the first law of thermodynamics at the isochoric process is $Q_v = \Delta U$* , where Q_v is the heat absorbed by the system in conditions of a constant volume.

The heat effect of a reaction at constant volume and temperature corresponds to the change in the internal energy of the system during the reaction. Or: *for a chemical reaction proceeding without a change in the volume of the system, a change in the internal energy equals the heat effect of the reaction taken with the opposite sign.*

The quantity Q_v , like U , is a function of state of a system.

The last equation ($Q = \Delta U$) allows us to determine the change in the internal energy in processes. For instance, when a substance is heated at constant volume, the change in the internal energy is determined from the heat capacity of this substance: $Q_v = \Delta U = nC_v\Delta T$, where C_v is the molar heat capacity of the substance at constant volume, n is the number of moles of the substance, and ΔT is the difference between the final and initial temperatures.

Examples of reactions proceeding at constant volume are reactions in a closed vessel (an *autoclave*), between solids and liquids without the evolution of gases, and between gases if their amount does not change.

2. *An isobaric process.*

For isobaric processes we have $p = \text{const}$ and $\Delta p = 0$, $A = p\Delta V$.

In case of isobaric process $Q_p = \Delta U + p\Delta V$;

$Q_p = U_2 - U_1 + pV_2 - pV_1$, where Q_p is the heat absorbed by the system at constant pressure.

Then we write $Q_p = (U_2 + pV_2) - (U_1 + pV_1)$.

With a view to the sign conventions adopted in thermodynamics, the work is positive if it is done on a system ($\Delta V < 0$) and negative if a system does work against the forces of its surroundings ($\Delta V > 0$).

The function $U + pV$ designated by H is called the enthalpy. The enthalpy, like the internal energy, is a function of state. The enthalpy has the dimension of energy. We obtain $Q_p = H_2 - H_1 = \Delta H$; $Q_p = \Delta H$.

The heat effect of a reaction at constant pressure and temperature corresponds to the change in the enthalpy of the system during the reaction.

The quantity Q_p , like Q_v , is a function of state of a system. *The enthalpy characterizes energy content of the system.*

The enthalpy, like the internal energy, characterizes the energy state of a substance, but includes the energy spent to overcome the external pressure, i.e. to do the work of expansion. Like the internal energy, the enthalpy is determined

by the state of a system and does not depend on how this state was reached. For gases, the difference between ΔU and ΔH in the course of a process may be considerable. For systems containing no gases, the changes in the internal energy and enthalpy attending a process are close to each other. The explanation is that the changes in the volume (ΔV) in processes occurring with substances in condensed (i.e. in the solid or liquid) states are usually very small, and the quantity $p\Delta V$ is small in comparison with ΔH .

The equation $Q_p = \Delta H$ allows us to determine the change in the enthalpy in different processes. Such determinations are similar to those of the internal energy, the only difference being that all the measurements must be conducted in conditions of a constant pressure. Thus, when a substance is heated, the change in its enthalpy is determined from the heat capacity of this substance at constant pressure. $\Delta H = Q_p = nC_p\Delta T$, where n is the number of moles of the substance, and C_p is its molar heat capacity at constant pressure.

3. An isothermal process

$T = \text{const}$ and then $\Delta U = 0$, and $Q_T = A$ i. e. heat transforms into the work of expansion $A = p\Delta V$.

4. An adiabatic process.

An adiabatic process is one in which the system doesn't change heat with its surroundings, the work is performed according decreasing of the internal energy of the system i. e. $Q = 0$, $Q = \Delta U + A$, $A = -\Delta U$.

3.4. Thermochemistry

Thermochemistry is the branch of chemical thermodynamics devoted to a quantitative study of the energy effects of chemical and physico-chemical processes.

The heat effect of a reaction is the amount of heat evolved or absorbed in a reaction. Reactions proceeding with the liberation (release) of energy are called *exothermic*, reactions in which energy is absorbed, *endothermic*.

The magnitude of the heat effect depends on the nature of the reactants (initial substances) and the reaction products, their state of aggregation and temperature.

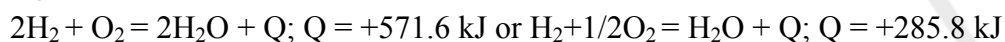
To be able to compare the heat effect of various reactions, one must indicate exactly the conditions under which these reactions occur, and also the physical state of each reaction component. Thermodynamic quantities are generally determined at *standard temperature and pressure (STP)*, namely, at $T = 298\text{K}$ (more exactly, 298.15K) and $p = 101\text{kPa}$ (more exactly, 101.325kPa).

The heat effect of a reaction is measured at a constant temperature (298K) and 101.325kPa (1atm) pressure for the formation of one mole of the product is called the standard heat effect of a reaction.

Heat effect can be included in the equations of reactions. Chemical equations in which the amount of liberated or absorbed heat is indicated are known as *thermochemical equations*. The physical state of the reactant and products are

indicated. The symbols of the elements and the formulas of substances indicate the amount of a substance, therefore the coefficients in thermochemical equations may be either integers or fractions.

There are two forms of writing thermochemical equations. The first form of writing is



where Q is the thermochemical heat effect of reaction which characterizes the energy change in the surroundings. If energy (E) flows from a system to the surroundings this process is called *exothermic* and $Q > 0$. If energy (E) flows into the system from its surroundings this process is called *endothermic* and $Q < 0$.

Another way to write this equation is $\text{H}_2 + 1/2\text{O}_2 = \text{H}_2\text{O}; \Delta H = -286 \text{ kJ/mol}$, where ΔH is the thermodynamic heat effect of the reaction which reflects the energy changes in a reaction system. When $\Delta H < 0$, a reaction is *exothermic* and energy decreases in a system. When $\Delta H > 0$, a reaction is *endothermic* and energy increases in a system. In any case $Q = -\Delta H$.

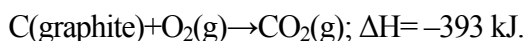
3.5. Hess's law

The fundamental principle on which all thermochemical calculations are based was established in 1840 by the Russian chemist, academician G.Hess. This principle is known as Hess's law and it is a particular case of the law of energy conservation. It can be formulated as follows:

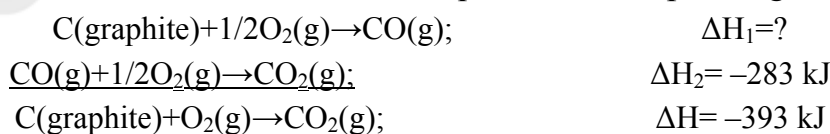
«The isochoric and isobaric heat effect of a reaction depends only on the initial and final state of substances and does not depend on the intermediate stages of the process».

Hess's law allows us to calculate the heat effects of reactions when for some reason or other they cannot be measured directly. Let us consider as an example of such calculations the determination of the heat of formation of carbon monoxide from graphite and oxygen. It is very difficult to measure the heat effect of the reaction $\text{C}(\text{graphite}) + 1/2\text{O}_2(\text{g}) = \text{CO}(\text{g})$, because upon the combustion of graphite in a limited amount of oxygen, what is obtained, is not only carbon monoxide, but its mixture with carbon dioxide. But the heat of formation of CO can be computed if we know its heat of combustion (283 kJ/mol) and the heat of formation of carbon dioxide (393 kJ/mol).

The combustion of graphite is expressed by the thermochemical equation

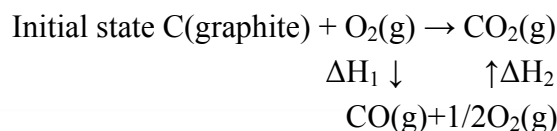


To calculate the heat of formation of CO, we shall write this reaction as two stages and summarize the thermochemical equations corresponding to these stages



The above transformations can be depicted schematically as follows:

ΔH



By Hess's law, $\Delta\text{H} = \Delta\text{H}_1 - \Delta\text{H}_2$. This enables us to find the value of ΔH_1 , which doesn't lend itself to experimental measurement, namely,

$$\Delta\text{H}_1 = \Delta\text{H} - \Delta\text{H}_2 = -393 - (-283) = -110\text{kJ}.$$

The heat effect of oxidation of glucose in the living organism and in the bomb calorimeter is the same!

The thermodynamical substantiation of Hess's law. Hess's law was established before the first law of thermodynamics. So Hess's law is a corollary of the first law of thermodynamics.

According to the first law of thermodynamics $Q_V = \Delta U$. ΔU doesn't depend on the path by which the system is brought from one state to the other. ΔU is a function of state. In this case Q_V doesn't depend on intermediate stages of proceeding of process as well.

$Q_p = \Delta H$, but ΔH doesn't depend on intermediate stages of proceeding of process, and in this case Q_p doesn't depend on intermediate stages of proceeding either.

$Q_T = A$, but work is not a function of state and it is a function of process.

Hence, Hess's law is strictly valid only for constant-volume processes (the isochoric processes) or for constant-pressure processes (isobaric processes). For these processes it is easily deduced from the first law of thermodynamics.

The corollaries of Hess's law. The physical state in which a pure substance is the most stable at $p = 101\text{kPa}$ and a definite temperature (most often 298 K) is assumed to be the standard state of this substance.

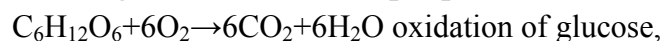
The standard enthalpy of formation of substance (ΔH_f°) is defined as the heat of the formation of one mole of a compound from its elements at standard conditions ($T = 298\text{ K}$, $p = 101\text{ kPa}$). Standard enthalpies of formation for the elements are defined as zero.

Standard enthalpies of combustion of substance ($\Delta H_{\text{com}}^\circ$) is defined as the heat effect of oxidation of one mole of a compound by oxygen to the higher oxides. Standard enthalpies of combustion of the higher oxides and oxygen are defined as zero.

It follows from Hess's law that:

1. *The enthalpy of formation of substance is equal to the enthalpy of decomposition of substance but opposite in sign, i. e. $\Delta H_f = -\Delta H_{\text{decomp}}$; (Law of Lavoisier and Laplace).*

2. *The heat effect of a reaction equals the sum of the standard enthalpies of formation of the products minus the sum of the standard enthalpies of formation of the reactants taking into account the proper stoichiometric coefficients.*



$$\Delta H_{\text{rxn}}^\circ = [6\Delta H_f^\circ(\text{CO}_2) + 6\Delta H_f^\circ(\text{H}_2\text{O})] - [\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6) + \Delta H_f^\circ(\text{O}_2)] = -2800\text{kJ},$$

$$\Delta H^\circ(\text{O}_2)=0,$$

$$\Delta H^\circ_{\text{rxn}}=\sum(m\Delta H^\circ_f)\text{prod.}-\sum(n\Delta H^\circ_f)\text{ react.},$$

where **m** and **n** are the coefficients in the equation of the reaction.

3. The heat effect of a reaction equals the sum of the standard enthalpies of combustion of the reactants minus the sum of the standard enthalpies of combustion of the products taking into account the stoichiometric coefficients.

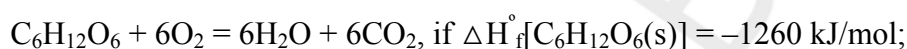
$$\Delta H^\circ_{\text{rxn}}=\sum(m\Delta H^\circ_{\text{com}})\text{ react.}-\sum(n\Delta H^\circ_{\text{com}})\text{ prod.},$$

subscript «rxn» is an abbreviation for «reaction».

3.6. Thermochemical calculations and their using for characteristics of biochemical processes

The values of the standard enthalpies is in the reference books. These values are used for the calculations.

Example. Calculate the heat effect of the reaction of oxidation of glucose.



$$\Delta H^\circ_f[\text{CO}_2(\text{g})] = -393.5 \text{ kJ/mol}; \Delta H^\circ_f[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ/mol}.$$

Solution:

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= (6\Delta H^\circ_f[\text{H}_2\text{O}(\text{l})] + 6\Delta H^\circ_f[\text{CO}_2(\text{g})]) - \Delta H^\circ_f[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] = \\ &= [6(-285.8) + 6(-393.5) - (-1260)] = -2815.8 \text{ kJ/mol}. \end{aligned}$$

It is known, the oxidation of one mole of glucose is attended by evolving of 2800kJ of energy in the process of vital activity of organism. The $\approx 80\%$ of this energy distributes into the surroundings in the form of heat, the $\approx 20\%$ of this energy is consumed for work (electrical, chemical, etc).

Thermochemistry is a theoretical base for a dietology. The thermochemical properties of foods are discussed in terms of their *specific enthalpy*, the magnitude of the enthalpy of combustion per gram of matter. The specific enthalpy of carbohydrates, which are the main source of energy for a human body, is about 6.7 kJ/g.

Specific enthalpy of lipids is much greater, at around 37.6 kJ/g. Lipids are commonly used as an energy store, to be used only when the more readily accessible carbohydrates have fallen into short supply.

Proteins are also used as a source of energy, but their components, the amino acids, are often too valuable to squander in this way, and are used to contract other proteins instead. When proteins are oxidized to urea, the equivalent specific enthalpy is comparable to that of carbohydrates (16,7 kJ/g).

Various foods have different compositions and hence different energy contents. Many labels on food packages show the calorie content of the food. The calorie (cal) is a non-SI unit of energy where 1 cal = 4.184 J (1 kcal = 4.184 kJ).

Daily Requirements in Energy depend upon muscle activity of a person:

1. Easy muscle work — 2500 kcal,
2. Average muscle work (students, doctors and some others) — 3500 kcal,

3. Hard muscle work — 4500 kcal,
4. Especially hard muscle work (sportsmen) — 7000 kcal.

High muscle activity increases energy requirements by 30–50 %. They are also increased by serious diseases of patients. Thus rheumatoid arthritis gives increase in energy requirements up to 10 %. High mental activity doesn't require increase in energy. Brain constantly oxidizes 5–6 g of glucose.

Table 3.1

Fuel values of food products

Food product	Content, %				Heat content kJ/kt
	Proteins	Lipids	Carbohydrates	H ₂ O	
Bread	6,3	1,3	46,1	43,9	9500
Noodle	11,0	0,9	74,2	13,6	14 980
Suger	—	—	99,9	0,1	17 150
Butter	0,5	83,0	0,5	16,0	32 470
Beaf	18	10,5	—	71,3	7150
Potatoes	2,0	—	21,0	76	3930
Apples	0,4	—	11,3	87	2130

Increase in energy of food products and decrease in physical activity is responsible to obesity. Obesity is a non inflectional Epidemic of the 21 century. 300 millions people suffer from obesity in the world. In high developed countries their number is 30 % of the total population. Obesity increases the risk of heart and oncological diseases, diabetes mellitus.

3.7. The second law of thermodynamics

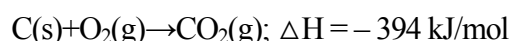
The multitude of different processes which take place in the world about us — in nature, technology, etc. — can be divided in two groups: *spontaneous and non-spontaneous processes*.

1. *The physical and chemical processes that occur without the outside energy are called spontaneous processes.*

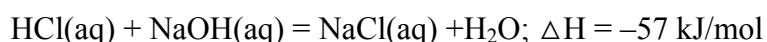
Examples of the spontaneous processes are: the fall of a sphere, the mixing of gases, the neutralization of a strong acid by a strong base, any of the reactions occurring during the work of an electrochemical cell, the combustion of fuel, the detonation of an explosive, the rusting of iron, the transformation of a substance from the glassy to the crystalline state, etc.

Majority of the spontaneous processes are exothermic reactions because there is decrease in energy. Examples of the spontaneous exothermic reactions:

a) burning of a substance:



b) neutralization of an acid with a base:



However, many spontaneous reactions may be endothermic. For example, dissolving NH_4NO_3 in water.

2. *The physical and chemical processes that occur with the outside energy are called non-spontaneous processes.*

In non-spontaneous processes work must be done on the system in an amount directly proportional to the change which is brought about.

Examples of non-spontaneous processes are: a separation of a mixture of gases, the motion of a sphere on an inclined plane upwards, the dissociation of water by an electric current, etc.

Changes that are spontaneous in one direction are non-spontaneous in the opposite direction.

The first law, as we have seen, states that the internal energy of an isolated system is constant, and that transformations between different forms of energy take place in equivalent amounts. This can also be expressed in the form of a relation between the change in the internal energy of a system, the amount of heat supplied to it, and the work performed. The first law, however, says nothing about the character, permissibility or direction of the processes by which the various conversions of energy are brought about.

The second law on the other hand, specifies what processes in the system of interest at given temperature, pressure, concentrations, etc., can occur spontaneously (i. e., without work being done on the system), what amount of work can be obtained from such processes, and what is the limit of the spontaneous process, i. e., to what state of equilibrium the system tends under the given conditions.

The second law allows us to indicate the external conditions necessary for the process of interest to proceed in the desired direction and to the required extent. For processes in which work must be done we can determine by means of the second law the amount of work required for the process to be carried out and the dependence of this quantity on the external conditions.

All this is of very great importance both for theoretical investigations in physical chemistry, and for the solution of various practical problems.

The second law of thermodynamics has a more limited field of application than the first law. It is of a statistical nature and is therefore applicable only to systems composed of a large number of particles, i.e. to systems whose behaviour can be described by the laws of statistics.

The changes in energy are not the only criterion for deciding the spontaneity of a reaction. The spontaneous processes lead to an equilibrium in a system as the final result. The quantitative measure of approach of the system to the equilibrium is *entropy (S)*.

This function is introduced by the second law of thermodynamics.

Entropy is a measure of the degree of disorder of a system. When disorder increases, entropy also increases. The entropy, like the enthalpy and internal energy, is a function of state of a system, hence the change in the entropy ΔS during the transformation of a system is determined only by the initial and final

states of the system, its temperature and pressure and does not depend on the path of the process.

For isolated systems, a change in the entropy is a criterion determining the direction of a process. *By the second law of thermodynamics in isolated systems the entropy of a spontaneous process increases, i. e. $\Delta S > 0$.*

In a closed system, the entropy may either increase or decrease during a process. It increases when a system passes from a more ordered state into a less ordered one.

The reverse transition of a system causes its entropy to diminish. *When the entropy is maximum the system is in condition of complete thermodynamic equilibrium ($\Delta S = 0$).*

The processes for which $\Delta S > 0$ include the expansion of gases, phase transitions during which a substance transforms from the solid to the liquid and gaseous states, and the dissolution of crystalline substances. The processes for which $\Delta S < 0$ include the compression of gases and the condensation and crystallization of substances.

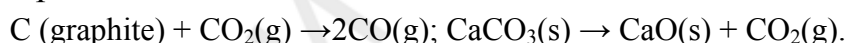
Gaseous state is the most disordered and so has the highest entropy. Liquid state is less ordered and so has less entropy than the gaseous state. Solid state is the most ordered and so has the lowest entropy.

$$S(\text{solid}) < S(\text{liquid}) < S(\text{gas}).$$

The second law of thermodynamics will be expressed by the following expressions: $\Delta S > 0$, that S is positive for an irreversible spontaneous change;

$\Delta S = 0$, that S is zero for a reversible change.

In a chemical reaction, the entropy grows if the volume of the system increases. Examples are the reactions:



A decrease in the volume in a reaction is attended by a decrease in the entropy, e. g. $2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$.

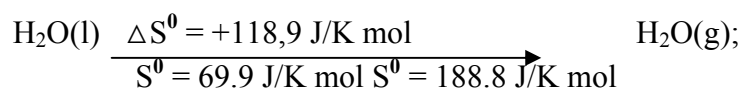
Unlike H and U, we can determine the absolute values of the entropy for all pure substances at any temperatures. By the third law of thermodynamics, the entropy of pure substances existing in the form of perfect crystals is zero at 0K. In other words, at absolute zero, complete order sets in in a perfect crystal.

The *standard entropy* of pure substances is determined for one mole of a substance at $p = 101.325 \text{ kPa}$ and a definite temperature, generally 298 K. It is designated by S^0_{298} or S^0 . The unit of the entropy is $\text{J/mol} \cdot \text{K}$.

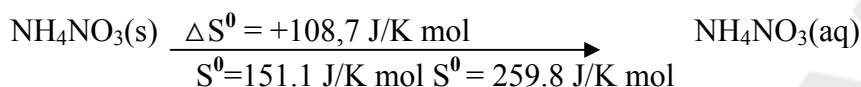
The standard entropy of simple substances does not equal zero.

The greater the disorder or randomness in a system, the larger the entropy.

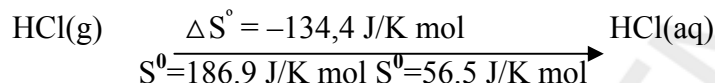
1. The entropy of a substance increases as it changes from solid to liquid to gas:



2. When pure solids or liquids dissolve in a solvent, the entropy of the substance increases.



3. When a gas dissolves in a solvent, its entropy declines.



A gas is clearly the most disordered state. When the substance dissolves, there are intermolecular interactions that impose some order, and the entropy declines.

4. Entropy generally increases with increasing molecular complexity.

There are several aspects to the relation between molecular complexity and entropy. For example, the standard entropy increases as the number of ions per formula unit in an ionic solid increases.

	KCl(s)	CaCl ₂ (s)	GaCl ₃ (s)
S ⁰ (J/K mol)	83	115	142

Similarly, entropy increases as the number of atoms increases in a related series of molecules.

In the following series of straight-chain hydrocarbons (all C atoms are bound into a non branching chain), notice that the entropy increases by about 40 J/K mol every time another –CH₂– group is added to the chain.

		S ⁰ (J/K mol) for gaseous compound
Methane	CH ₄	186.3
Ethane	C ₂ H ₆	229.6
Propane	C ₃ H ₈	269.9
Butane	C ₄ H ₁₀	310.0
Octane	C ₈ H ₁₈	463.6.

A corollary to this is that entropy increases when going from a three-dimensional network solid to one that is only two dimensional. The best examples are of course diamond and graphite, whose very low entropies reflect the high degree of order.

	S ⁰ J/K mol
Diamond	2.38
Graphite	5.74
Quarts(SiO ₂)	41.8.

In general, elements that have a high degree of covalent bonding in the solid state (B, C, P, S) have relatively low standard entropies. Metals have values ranging from about 10 J/K mol to 80 J/K mol, while the gaseous elements have the highest values of all.

Since the entropy is a function of state, the change in the entropy ΔS attending a chemical reaction equals the difference between the values of the absolute entropies of the products and reactants at the temperature and pressure of the reaction. For a chemical reaction at standard temperature and pressure (**STP**) we have:

$$\Delta S^0_{\text{rxn}} = \sum m S^0_{\text{prod.}} - \sum n S^0_{\text{react}}$$

where m and n are the number of moles of products or reactants, respectively.

3.8. The statistical interpretation of entropy

The statistical interpretation of entropy is based on the kinetic theory of gases.

Consider a system containing about five molecules. Every molecule has its own number. Take photograph of this system and have a photo. Then, take another photograph of this system and have another photo, etc. After all we conclude that a macrostate is the state of substance characterized by definite values of its macroscopic properties (temperature, pressure, volume, etc.); a microstate is the state of substance characterized by a definite state of each particle (molecule, atom). The same macrostate corresponds to a great number of various microstates. The number of microstates that form given macrostate is called *the thermodynamic probability* of the given state of the system (**W**)

If $W = 1000$ it means that one macrostate corresponds to 1000 microstates. (The thermodynamic probability should not be confused with mathematical probability which is not greater than one).

There is a relation between entropy and thermodynamical probability of the system (*Boltzmann's equation*):

$$S = k \ln W,$$

where k is a constant in energy or is Boltzmann's constant $k = \frac{R}{N_A}$, where R is the molar gas constant equal to 8.314 J/mol K; N_A is Avogadro's number equal to $6.02 \cdot 10^{23} \text{ mol}^{-1}$. $k = 1,38 \cdot 10^{-23} \text{ J/K}$.

Greater the thermodynamic probability of the given system, greater will be entropy.

3.9. The thermodynamical interpretation of entropy

If the statistical interpretation of entropy is given by L. Boltzmann, the thermodynamical interpretation of one is given by Clausius.

We know the entropy of a pure perfectly ordered crystalline substance is zero at the absolute zero of temperature ($S = 0$). In this case one macrostate corresponds to one microstate ($W = 1$), that is $S = 0$ and a system is in equilibrium ($\Delta S = 0$).

With elevation of the temperature the entropy increases, the thermodynamic probability increases but the order decreases in the system. So the entropy

of a system depends on quantity of energy (**Q**) put into a system and temperature (**T**) at which the process is carried out. The change in entropy is related to the heat absorbed by the equation:

$$\Delta S_{\text{sys}} \geq Q_{\text{sys}}/T.$$

It is a mathematical expression of the second law of thermodynamics. *For processes with the system at equilibrium:*

$$\Delta S_{\text{sys}} = Q_{\text{sys}}/T \quad (3.1)$$

According to equation $\Delta S_{\text{sys}} = Q_{\text{sys}}/T$ in reversible isothermal processes the entropy change is equal to the heat of the process divided by the absolute temperature.

For a spontaneous process:

$$\Delta S_{\text{sys}} > Q_{\text{sys}}/T \quad (3.2).$$

This equation makes an important distinction between equilibrium and non-equilibrium systems; spontaneously changing systems experience greater disorder (3.2) than they would if the change were made under equilibrium conditions (3.1).

Proteins are formed in the living organisms from amino acids. The process is attended with the decreasing of entropy and consequently the proteins are higher ordered systems.

Synthesis of DNA, RNA proceeds with the decreasing of entropy as well. They are non-spontaneous processes. These processes are needed in energy.

The living organism is an open system which changes energy and matter with its surroundings.

We must consider the living organism as an open system with its surroundings. In this case $\Delta S_{\text{sys}} + \Delta S_{\text{sur}} > 0$. It is impossible to apply the second law of thermodynamics for living organism without biological processes as well.

3.10. The gibbs free energy

In order to know about direction and limit of the processes in opened and closed systems it is necessary to take account of change in entropy of surroundings. It is very complex and sometimes impossible task.

Besides the change in the enthalpy in the course of a chemical reaction is not a criterion of its direction. Both exothermic and endothermic reactions may proceed spontaneously, although the latter are fewer in number under ordinary conditions.

Consequently the possibility of processes occurring in closed and opened systems at constant temperature and pressure is determined by the change in a thermodynamic function of state called the *Gibbs free energy* ΔG , which is related to the enthalpy and entropy by the equation:

$$G=H -TS, \quad (3.3)$$

where T is the absolute temperature. Synonyms of the Gibbs free energy are the isobaric — isothermal potential, isobaric potential, and the free energy at constant pressure.

The change in the Gibbs energy shows how the direction of a chemical reaction is affected by two competing trends simultaneously acting in a system, namely (3.1) the trend to a minimum energy, and (3.2) the trend to a maximum entropy. At constant temperature and pressure, the change in the Gibbs energy is:

$$\Delta G = \Delta H - T\Delta S \quad (3.4).$$

The notion about the Gibbs energy was introduced on the basis of equations of the first law and second law of thermodynamics.

The equation for the first law of thermodynamics is

$$Q = \Delta U + A \quad (3.5),$$

the equation for the second law of thermodynamics is

$$\Delta S = Q/T, \text{ or } Q = T\Delta S \quad (3.6)$$

Inserting in the expression (3.5) the value $Q = T\Delta S$ from (3.6) we obtain:

$$T\Delta S = \Delta U + A \quad (3.7).$$

The system can perform not only the work of expansion ($p\Delta V$) but perform another forms of work (electric, chemical, osmotic, etc.)

Write the maximum work of process (A_{\max})

$$-A_{\max} = p\Delta V + A_u \quad (3.8),$$

where A_u is the maximum useful work.

Comparing equations (3.7) and (3.8) we obtain

$$\begin{aligned} T\Delta S &= \Delta H + p\Delta V + A_u \\ -A_u &= \Delta U + p\Delta V - T\Delta S \\ -A_u &= U_2 - U_1 + pV_2 - pV_1 - TS_2 + TS_1 \\ -A_u &= \underbrace{(U_2 + pV_2 - TS_2)}_{H_2} - \underbrace{(U_1 + pV_1 - TS_1)}_{H_1} \\ -A_u &= (H_2 - TS_2) - (H_1 - TS_1); H - TS = G \quad (3.9) \\ -A_u &= G_2 - G_1 = \Delta G \\ -A_u &= \Delta G \quad (3.10) \end{aligned}$$

In the reversible and isothermal conducting of a process, ΔG is equal in magnitude, but opposite in sign, to the maximum useful work that the system does in the given process.

By useful work is meant all the work done in the course of a process less the work of expansion $p\Delta V$.

It follows from equation $A_u = -\Delta G$ that if a system performs work spontaneously ($A > 0$), then $\Delta G < 0$. In this case a criterion of a spontaneous process is:

$$A > 0 \text{ or } \Delta G < 0.$$

If the system doesn't perform work then $A = 0$ and $\Delta G = 0$. *It is a criterion of equilibrium state.*

The unit of the Gibbs free energy is J/mol.

The enthalpy and entropy factors and direction of a process

$\Delta G = \Delta H - T\Delta S$. The sign and the magnitude of ΔG are determined by two factors: entropy ($T\Delta S$) and enthalpy (ΔH).

The enthalpy factor defines the tendency of a system to its minimum of energy.

The entropy factor defines the tendency of a system to its disorder.

The Gibbs free energy is an integral function of state of a system.

Depending on the temperature, the influence of one of these factors on the value and sign of ΔG and consequently on the direction of a process may be determining the table 3.2.

Table shows the possibility (or impossibility) of the spontaneous proceeding of a reaction with different combinations of the signs of ΔH and ΔS .

1. If $\Delta H < 0$ for a reaction (an exothermic reaction), and $\Delta S > 0$, it follows from the equation $\Delta G = \Delta H - T\Delta S$ that at all temperatures $\Delta G < 0$. This signifies that the reaction can proceed spontaneously at any temperatures.

The exothermic reactions attended by an increase in the entropy can proceed spontaneously. $\Delta H < 0$, $\Delta S > 0$, $\Delta G < 0$

Table 3.2.

Directions of reactions with different signs of ΔH and ΔS

Sing of change in function			Possibility (impossibility) of spontaneous proceeding of reactions
ΔH	ΔS	ΔG	
-	+	-	Possible at any temperature
+	-	+	Impossible at any temperature
-	-	\pm	Possible at sufficiently low temperature
+	+	\pm	Possible at sufficiently high temperature

2. If $\Delta H > 0$ (endothermic reaction) and $\Delta S < 0$ it follows from the equation $\Delta G = \Delta H - T\Delta S$ that $\Delta G > 0$. *The endothermic reactions attended by a decrease in the entropy and the process can't proceed spontaneously:* (at an ordinary temperature and atmospheric pressure). ($\Delta H > 0$, $\Delta S < 0$, $\Delta G > 0$)

3. If $\Delta H < 0$ and $\Delta S < 0$ or $\Delta H > 0$ and $\Delta S > 0$. In this case value of ΔG depends on absolute values of ΔH and $T\Delta S$: if $|T\Delta S| > |\Delta H|$ then $\Delta G < 0$; if $|T\Delta S| < |\Delta H|$ then $\Delta G > 0$.

If $\Delta H < 0$ and $\Delta S < 0$, the reaction is possible ($\Delta G < 0$) provided that the term ΔH in the equation for the Gibbs energy is greater in magnitude than the term $T\Delta S$; since the magnitude of the term $T\Delta S$ increases with a growth in the factor T , this condition will be observed at sufficiently low temperatures.

In other words, at low temperatures, the spontaneous proceeding of exothermic reactions is most probable even if the entropy of the system diminishes.

At high temperatures, as can be seen from the table, reactions attended by a growth in the entropy are most probable, including endothermic reactions.

We must add that a negative value of ΔG for a reaction points only to the possibility of its occurring. Actually, the reaction may not be observed. The matter is that its rate may be low; hence, notwithstanding observance of the condition $\Delta G < 0$, the reaction will virtually not proceed. In these cases, an appropriate catalyst must be found to increase the rate of the reaction. Such cases are especially frequent at low temperatures.

4. If $\Delta H = T\Delta S$, then $\Delta G = 0$ and the equilibrium sets in (is settled) in the system.

Calculation of ΔG^0 in chemical reactions:

1. The standard free energy of formation ΔG_f^0 is the change of free energy during the formation of a substance in its standard state from the elements in their standard states. The standard free energies of formation of elements in their standard states are zero. The free energy change for a reaction can be found from values of ΔG_f^0 by general equation.

$$\Delta G_{\text{rxn}}^0 = \sum m \Delta G_f^0 \text{ prod.} - \sum n \Delta G_f^0 \text{ react.},$$

where m and n are the numbers of moles of a given product or reactant, respectively.

But the reactions don't proceed at standard conditions (the concentration can not be 1mol/liter).

2. For the reaction $A+B=C+D$ in real conditions calculation of ΔG can be performed according to the equation:

$$\Delta G_{\text{rxn}} = \Delta G^0 + RT \ln [C][D]/[A][B],$$

where $[C]$, $[D]$, $[A]$ and $[B]$ are the concentrations of the substances; ΔG^0 is the standard change in the Gibbs energy of the reaction, R is the molar gas constant

($R = 8.314 \text{ Jmol/K}$); T is the temperature, K .

3. Alternatively, you can calculate the enthalpy and entropy changes for the reaction ΔH_{rxn}^0 and ΔS_{rxn}^0 and combine them using the Gibbs equation:

$$\Delta G_{\text{rxn}}^0 = \Delta H_{\text{rxn}}^0 - T\Delta S_{\text{rxn}}^0$$

$$\Delta H^{\circ}_{\text{rxn}} = \sum \Delta H^{\circ}_{\text{prod.}} - \sum \Delta H^{\circ}_{\text{react.}}$$

$$\Delta S^{\circ}_{\text{rxn}} = \sum S^{\circ}_{\text{prod.}} - \sum S^{\circ}_{\text{react.}}$$

a) $\Delta G^{\circ} < 0$ (is less than zero), a process is spontaneous at standard conditions;

b) $\Delta G^{\circ} > 0$ (is greater than zero), a process is not spontaneous at standard conditions;

c) $\Delta G^{\circ} = 0$, the process is at equilibrium.

3.11. Bioenergetics. Endergonic and exergonic reactions

Bioenergetics is thermodynamics of biological systems. It deals with the energy, heat and work exchange in plants, animals and human bodies. A human body is an open stationary system. Its main source of energy is chemical energy of food products (99 %). Carbohydrates are responsible for 55–60%, lipids — 20–25 %, and proteins — 15–20 %.

In general efficiency of food chemical energy conversion in a human body is approximately 20–25 %. Thus waste energy dissipated into surroundings is 75–80 %. 20 liters of water can be boiled if focused daily waste energy of one person. Biochemical reactions are chemical reactions which proceed *in vivo*. They are:

Exergonic (spontaneous) $\Delta G < 0$;

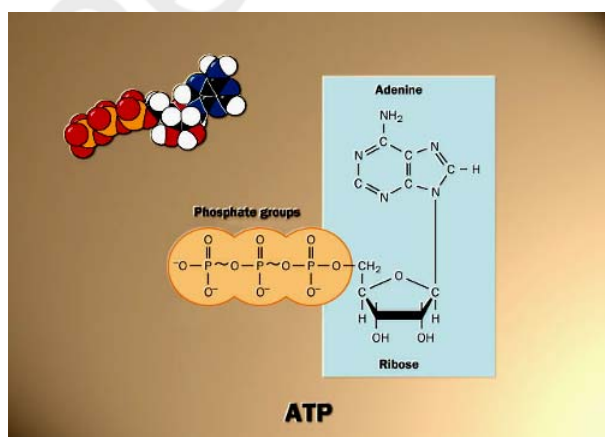
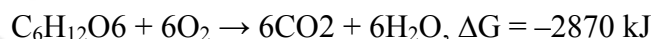
Endergonic (nonspontaneous) $\Delta G > 0$.

Many biochemical reactions are endergonic, but in some cases they can be carried out to an appreciable extent by coupling them with an exergonic reaction.

A coupled (conjugated) reaction is a process in which an endergonic reaction is made to proceed by coupling it to an exergonic reaction. Biologically coupled reactions are usually mediated with the aid of enzymes. A scheme of a coupled reaction can be represented as follows:



Carbohydrates and lipids metabolism involves highly spontaneous oxidation reactions:



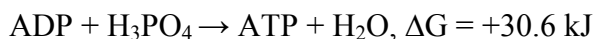
Some of this energy is released as heat that maintains constant body temperature. Another portion is stored in high-energy molecules that a body uses as «power sources» for numerous

reactions that occur within cells. The most important of these energy transport molecules is adenosine tri-phosphate (ATP) (fig.3.4).

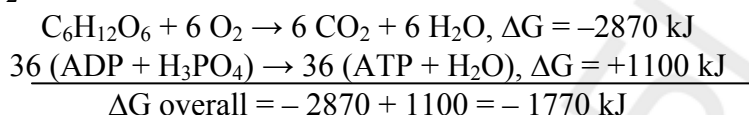
Adenosine triphosphate (ATP) is a high-energy triphosphate ester used in living systems to provide chemical energy for metabolic needs.

Fig. 3.4. The structure of ATP

Synthesis of ATP molecules from ADP and phosphoric acid is nonspontaneous under physiological conditions:



In cells ATP production is coupled with glucose oxidation. One molecule of glucose can convert as many as 36 ADP molecules into ATP molecules as it is oxidized to CO₂ and water:



Although 1100 kJ of energy is stored in this coupled process, 1770 kJ of energy is “wasted”. Efficiency of a process is: $1100/2870 = 0.38$ or 38%

Thus cells harness 38% of the chemical energy stored in glucose to drive the biochemical machinery of metabolism. The remaining 62% of energy is dissipated as heat.

3.12. Thermodynamics of the chemical equilibrium

All chemical reactions can be divided into two groups: *irreversible* and *reversible* reactions. *Irreversible reactions proceed to the end* — until one of the reactants is completely used up. Irreversible reactions are characterized by the formation of an insoluble substance, the formation of a gas, the formation of a weak electrolyte (H₂O).

A reversible reaction is the reaction which can proceed either in the forward or in the reverse direction. Reversible reactions are characterized by the symbol \rightleftharpoons between the reactants and products. When the rates of the forward (V_f) and reverse (V_r) reactions become the same, *chemical equilibrium sets in*, i. e. $V_f = V_r$. As soon as equilibrium has been reached, the concentrations of the substances (both the reactants and the products) remain unchanged provided the conditions are not altered. These concentrations are called *equilibrium concentrations*.

Chemical equilibrium is characterized quantitatively by a quantity known as the chemical equilibrium constant. *The chemical equilibrium constant is the ratio of the product of product equilibrium concentrations to the product of reactant equilibrium concentrations.* For example, for the reaction $aA + bB \rightleftharpoons cC + dD$ the chemical equilibrium constant is:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Concentrations of solids are assumed to be 1 and they can be left out of the concentration ratio without altering the value of K .

The numerical value of the equilibrium constant in the first approximation characterizes the yield of the given reaction (the yield of a reaction is defined as the ratio of the amount of a substance produced to its amount that would have been produced if the reaction proceeded to the end). For example, when $K \gg 1$, the yield of a reaction is high, because $[C]^c [D]^d \gg [A]^a [B]^b$ i.e. at equilibrium, the concentrations of the products are much greater than those of the reactants, and this is exactly what signifies that the yield of the reaction is high. When $K \ll 1$ the yield of the reaction is low.

The magnitude of the equilibrium constant depends on the nature of the reacting substances and on the temperature. It does not depend on the presence of catalysts. A catalyst does not affect the magnitude of the equilibrium constant and, consequently, cannot either increase or lower the yield of the reaction. It can only accelerate or retard the setting in of equilibrium.

The equilibrium constant determines the extent of a process by the instant of reaching the equilibrium state. The larger this quantity, the greater is the degree of conversion of the reactants into the products.

The ways of designation of the equilibrium constant:

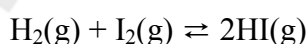
1. For solutions of non-electrolytes and sufficiently dilute solutions of electrolytes the equilibrium constant K_c is used (the equilibrium concentrations are expressed in mol/liter in liquid phase):

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

2. For strong electrolytes the activity (a) is used:

$$K_a = \frac{a^c(C) \cdot a^d(D)}{a^a(A) \cdot a^b(B)}$$

3. Chemical equilibrium between gases at low pressures is expressed in terms of the partial pressures p_i of the reactants and products:



$$K_p = \frac{p^2(HI)}{p(H_2) \cdot p(I_2)}$$

A relationship between K_c and K_p is given by an equation:

$$K_c = K_p \cdot RT^{(a+b-c-d)}$$

3.13. The equation of the isotherm of a chemical reaction

$A + B \rightleftharpoons C + D$. The reaction takes place at constant temperature and constant pressure.

The change in the Gibbs energy of this reaction in real conditions is

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C][D]}{[A][B]} \quad (3.11)$$

The value of the change in the Gibbs energy in a reaction depends on the temperature and also on the nature and concentrations of the reactants and products.

For the state of chemical equilibrium $\Delta G=0$, then we obtain from (3.11)

$$0 = \Delta G^\circ + RT \ln \frac{[C][D]}{[A][B]}, \text{ but } \ln \frac{[C][D]}{[A][B]} = \ln K_c \text{ and } \Delta G^\circ = -RT \ln K_c \quad (3.12)$$

We can write this equation (3.12) as $\ln K_c = -\Delta G^\circ/RT$ or in exponential form

$$K_c = e^{-\Delta G^\circ / RT} \quad (3.13),$$

where e is the base of natural logarithms ($e = 2.718\dots$).

From equation (3.13) we can deduce, that K_c depends on the temperature and the nature of the reactants (entropy and enthalpy factors).

With elevation of the temperature the equilibrium constant increases too.

The $\ln K_c$ determines the extent of a proceeding of a reaction.

K_c is the equilibrium constant expressed in terms of concentrations of the components A,B,C, and D in equilibrium.

If we introduce the value 2.303 (the number 2.303 is coefficient of transition from natural logarithm to common one) and the value of the molar gas constant $R=8.31 \text{ J/mol K}$ into the above equation (3.12), we get

$$\Delta G^\circ = -2.303 \cdot 8.31 \cdot T \log K_c = -19,1 \log K_c \text{ (J/mol)}$$

$$\text{or } \Delta G^\circ = -0,0119 \cdot T \log K_c \text{ (kJ/mol)}$$

Introduce the equation (3.12) into the equation (3.11), we get

$$\Delta G = -RT \ln K_c + RT \ln \frac{[C][D]}{[A][B]} \quad (3.14),$$

where $[A],[B], [C], [D]$ are not equilibrium concentrations. It is the equation of the isotherm of a chemical reaction, where $\ln \frac{[C][D]}{[A][B]}$ is the concentration term; $\ln K_c$ is the constant term.

The sign of ΔG depends on the real concentrations of the reactants and products for given time (for a moment).

The analysis of the equation (3.14):

1. $\ln \frac{[C][D]}{[A][B]} < \ln K_c$ and $\Delta G < 0$

A spontaneous chemical reaction occurs from left to right. If we change the concentrations we can affect the direction of the spontaneous proceeding of the reaction.

2. $\ln \frac{[C][D]}{[A][B]} > \ln K_c$ and $\Delta G > 0$

A spontaneous chemical reaction doesn't occur from left to right, but the reaction is spontaneous from right to left.

$$3. \ln \frac{[C][D]}{[A][B]} = \ln K_c \text{ and } \Delta G = 0$$

The system is in an equilibrium.

The equation $\Delta G^\circ = -19,1 \lg K_c$ makes it possible to calculate the equilibrium constant, if we know ΔG° and, conversely, to determine ΔG° for a reaction using the experimentally found value of the equilibrium constant. It must be stressed in this connection that the sign of ΔG° indicates the possibility or impossibility of a reaction proceeding only in standard conditions, when all the reactants and products are in standard states.

In the general case, however, the possibility (or impossibility) of a reaction is determined by the sign of ΔG , and not of ΔG° .

The equilibrium constant's dependence on the enthalpy and entropy factors indicates that it also depends on the nature of the reactants.

3.14. The equation of the isobar of a chemical reaction

$p = \text{const}$, in the integral form we have the equation:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (3.15),$$

where K_1 and K_2 are equilibrium constants at the different temperatures T_1 and T_2 ; ΔH is change in enthalpy; R is the molar gas constant.

This equation relates the equilibrium constant, the enthalpy change and the temperature, i.e. it relates the kinetics and thermodynamics.

$$\text{The equation is in the differential form } \frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2} \quad (3.16)$$

These equations (3.15 and 3.16) establish a relation between the change in the equilibrium constant with temperature and the heat of the reaction. They are valid for processes which take place at constant pressure, and are called *the equations of the reaction isobar*.

For constant-volume processes a similar equation can be obtained:

$$\frac{d \ln K_c}{dT} = \frac{\Delta U}{RT^2} \quad (3.17),$$

This equation relates the change in the equilibrium constant with temperature to the heat of the reaction and is called *the equation of the reaction isochore*. ΔU is the change in internal energy.

The analysis of the equation of the Isobar of a chemical reaction (3.16):

1. $\Delta H < 0$ *exothermic reaction*.

When heat is evolved in the chemical reaction i. e. $\Delta H < 0$ and $\frac{\Delta H}{RT^2} < 0$ as

well, then from equation (3.16) we conclude that $\frac{d \ln K_p}{dT} < 0$. This denotes that the equilibrium constant decreases with rise in temperature (the numerator de-

creases) and equilibrium is displaced towards the left. In other words, with rise in temperature equilibrium is displaced in the direction of the endothermic process.

With lowering in temperature the equilibrium constant increases ($dT < 0$) and equilibrium is displaced towards the right.

2. $\Delta H > 0$ endothermic reaction.

When heat is absorbed in the chemical reaction, i. e. $\Delta H > 0$ and $\frac{\Delta H}{RT^2} > 0$ as well, then from equation (3.16) we conclude that $\frac{d \ln K_p}{dT} > 0$. This denotes that the equilibrium constant increases with rise in temperature and with lowering in temperature the equilibrium constant decreases.

The equations (3.16) and (3.17) of the reaction isobar and isochore describe the change in the equilibrium constant with temperature. They express this dependence in differential form. For practical computations of equilibrium at different temperatures it is usually necessary to integrate these expressions.

3.15. Le chatelier principle

A change in the conditions (temperature, pressure, concentration) under which a system is in a state of chemical equilibrium disturbs equilibrium because of the different changes in the rates of the forward and reverse reactions ($V_f \neq V_r$). With time, new chemical equilibrium sets in in the system ($V_f = V_r$) that corresponds to the new conditions. The transition from one equilibrium state to another is called a *shift of equilibrium*.

The direction of a shift of chemical equilibrium as a result of a change in the external conditions is determined by *Le Chatelier's principle*: «if any change of conditions is imposed on a system in equilibrium, equilibrium will shift in the direction of the process that counteracts the imposed change».

For instance, *elevation of the temperature* leads to the shifting of equilibrium in the direction of the reaction attended by the absorption of heat, i. e. by cooling of the system;

an increase in the pressure causes equilibrium shift in the direction of a decrease in the total number of moles of gaseous substances, i.e. in the direction leading to lowering of the pressure;

the removal from a system of one of the products results in equilibrium being displaced in the direction of the forward reaction;

diminishing of the concentration of one of the reactants leads to shifting of equilibrium in the direction of the reverse reaction.

CHAPTER 4 CHEMICAL KINETICS

Chemical kinetics is the science about rates and mechanisms of chemical reactions. Tasks of chemical kinetics:

1. The establishment of factors affecting rates of chemical reactions.
2. The establishment of mechanism of chemical reactions.

4.1. Basic Concepts of chemical kinetics, simple and complex reactions

Simple reactions have one step and their stoichiometric equations exactly express the real process.

For example: $\text{H}_2 + \text{I}_2 = 2\text{HI}$

Complex reactions have several steps and their stoichiometric equations don't express the real process which consists from several steps.

For example: $\text{H}_2\text{O}_2 + 2\text{HI} = \text{I}_2 + 2\text{H}_2\text{O}$

The first step $\text{H}_2\text{O}_2 + \text{HI} = \text{HOI} + \text{H}_2\text{O}$

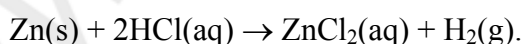
The second step $\frac{\text{HOI} + \text{HI} = \text{I}_2 + \text{H}_2\text{O}}{\text{H}_2\text{O}_2 + 2\text{HI} = \text{I}_2 + 2\text{H}_2\text{O}}$

Most reactions are complex. The mechanism of every chemical reaction is determined by the sum of steps. Every individual step of mechanism of chemical reaction is called a simple reaction.

Homogeneous and heterogeneous reactions. Homogeneous reaction refers to reaction occurring amongst species present in the same phase, or in liquid and gaseous solutions.

For example: $\text{N}_2 + \text{O}_2 \xrightarrow{t} 2\text{NO}$
 $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

When different phases occur, for example between two immiscible liquids or a solid and a liquid, the reaction is referred to as heterogeneous. The reaction can occur only at the surface of contact of the two phases:



4.2. Rates of reactions

Chemical reactions proceed at different rates. The reaction of neutralization between aqueous acids and bases occurs almost instantaneously, while the rusting of iron is slow.

The rates of chemical processes in vivo differ greatly. The time of the total renewal of bone tissue is 4–7 years, the time of a half proteins renewal — 70 days, chemical reactions responsible for neural activity run instantly.

The rate of chemical reaction is a basic concept in chemical kinetics.

The rate of a reaction can be measured by the change of molar concentration of one of the reactants or products per unit time .

The rate of chemical reaction can be calculated from the formula

$$v = \frac{\Delta C}{\Delta t} ,$$

where ΔC is the change of concentration in mole /liter; Δt is the change of time in sec., min., hour.

$$[V] = \left[\frac{\text{mol}}{\text{liter} \cdot \text{sec.}} \right] \text{ or } \left[\frac{\text{mol}}{\text{liter} \cdot \text{min}} \right].$$

This is an average rate of chemical reaction, i.e. the rate in the period of time from t_0 till t . The average rate is designated as \bar{V} . In practice the instantaneous rate is used. The instantaneous rate is the rate at the given moment of time (R).

The smaller the period of time Δt the nearer the average rate (\bar{V}) to the instantaneous rate (R), i.e. the average rate \bar{V} in the period of time from t_0 till t approaches t_0 the instantaneous rate of chemical reaction provided t leads to t_0 (provided $t \rightarrow t_0$) or mathematically:

$$R = \lim_{t \rightarrow t_0} \bar{V} = \lim_{t \rightarrow t_0} \left(\frac{\Delta C}{\Delta t} \right)$$

The instantaneous rate i.e. the rate at instant t_0 will be the limit of the average rate $\frac{\Delta C}{\Delta t}$ as t tends towards t_0 .

The ratio $\frac{\Delta C}{\Delta t}$ can go on to the infinitesimals and give derivative $\frac{dC}{dt}$, i. e. $R = \pm \frac{dC}{dt}$.

In the way the derivative from concentration (C) to time (t) characterizes the instantaneous rate (real rate) of chemical reaction.

Measurement of rate of a chemical reaction. Rate of reaction is always to be determined experimentally and cannot be predicted theoretically.

1. Direct methods.

The concentration of reactants or products is determined depending on time. By plotting C against t a graph of the type shown in the fig. 4.1, 4.2 is obtained. This graphs are called a Rate Curve.

Knowing the Rate Curve for any substance it is easy to calculate the rate of decomposition or formation of the substance by measuring slope as shown in fig. 4.1, 4.2. The slope of the Rate Curve characterizes the real rate at the given moment, i. e. the tangent α of slope numerically equals the real rate. Mathematically: $\text{tg}\alpha \approx \frac{\Delta C}{\Delta t} \approx \bar{V}$ (average rate). Tangent of α approximately equals the ratio of ΔC to Δt and equals the average rate, or in differential form: $\text{tg}\alpha = \frac{dC}{dt} = R$, α is the angle of slope of Rate Curve.

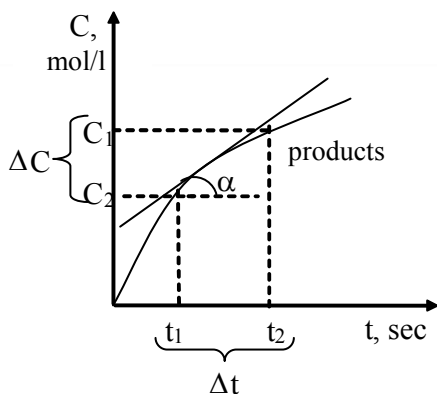


Fig. 4.1. The concentration increases

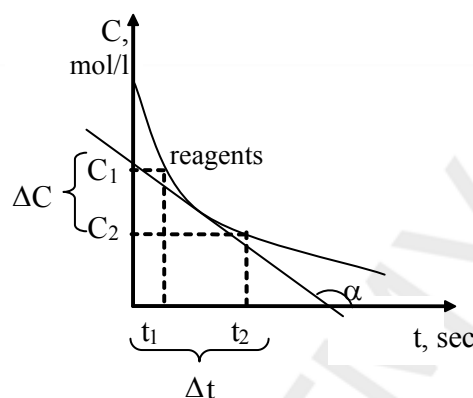


Fig. 4.2. The concentration decreases

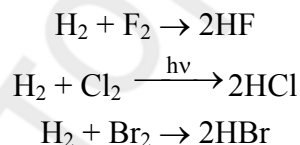
2. Indirect methods.

During a chemical reaction the concentrations of the reactants present change with time, and hence the properties of the reaction mixture are apt to change. The rate of the reaction is determined by measuring a changing property, such as intensity of colour, partial pressure of one component, refractive index, pH (negative common logarithm of H^+ concentrations), conductivity et al.

4.3. Factors influencing the rate of a reaction

Experimentally, the reaction rate is found to be affected by the following factors:

1. Nature of reactants



2. Effect of temperature

3. Effect of concentration

Experiment shows that the rate of a given reaction may be increasing the concentration of one or of all the reactants.

E. g. a very dilute aqueous hydrochloric acid solution reacts with zinc more slowly than a more concentrated solution of the acid. However, the quantitative influence of the concentration and how the reaction rate changes can be found only by experiment.

4. Effect of pressure (gaseous systems)

5. The form of vessel

6. Catalysts

The effect of concentration on the rate of chemical reaction. The effect of concentration on the rate of chemical reaction is expressed by basic postulate of chemical kinetics.

The rate of a chemical reaction (instantaneous) at a constant temperature is directly proportional to the product of the concentrations of the reactants to powers is expressed with small numbers.

Thus, for the reaction $mA + nB \rightleftharpoons C + D$ we have $V = k[A]^m[B]^n$, where V is the rate; k is the rate constant; and $[A]$ and $[B]$ are the concentrations of the reactants A and B ; m, n are small numbers. The equation reflecting the function connection between the rate of the reaction and concentration of the reactants is called kinetic equation where k is the rate constant:

$$V = \pm \frac{dC}{dt} = k[A]^m[B]^n,$$

Concentrations of solids are assumed to be 1 (constant) and they can be left out of kinetic equation.

Physical sense of k :

k is a such rate of the reaction when concentration of the reactants equal 1 mol/liter or product of this concentrations equal one, i. e. $\frac{dC}{dt} = k$ at $[A] = [B] = 1$ mol/liter.

Sometimes k is called the specific rate.

Chemical sense of k : the rate constant of the chemical reaction is quantitative measure of reaction ability of molecules.

The more k the more rate of the reaction.

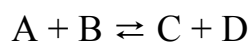
The rate constant doesn't depend on concentration of the reactants but depends on temperature.

Write equation: $V = k[A]^m[B]^n$, where m is the order with respect to reactant A , while n is the order with respect to reactant B . The sum $(m + n)$ is called the common (total) order of the reaction.

The order of the reaction is the formal magnitude and depends upon the concentration, the temperature, the catalyst. The order of the reaction can be positive, negative, whole or fractional numbers, nought.

The order of the reaction is determined by experimentally and it is not necessarily related to the equation written for the reaction. The order of the reaction cannot be predicted before.

Consider the balanced reaction between A and B to give C and D :



Assume that the reaction takes place in a container with a constant volume and of a constant temperature.

Take the substance A in excess and its concentration remains constant. Then we study the rate of the reaction to reactant B , changing its concentration.

$[B] \rightarrow V$ Then the order of the reaction

$2[B] \rightarrow 4V$ with respect to reactant B

$3[B] \rightarrow 9V$ is n , id est $2n = 2$

If we take the substance B in excess its concentration remains constant. Then we study the rate of the reaction to reactant A, changing its concentration.

$[A] \rightarrow V$ Then the order of the reaction

$2[A] \rightarrow 2V$ with respect to reactant A

$3[A] \rightarrow 3V$ is m, id est 1 $m = 1$

4.4. Classification of the reactions in order

1. Zero order reactions

Here the rate doesn't depend on the concentration. The rate is constant.

Kinetic equation is: $V = -\frac{dC}{dt} = k_0$,

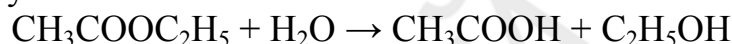
where k_0 is the rate constant, the units of k_0 are: $[k_0] = [C][t^{-1}] = [\text{mol} \cdot \text{liter}^{-1} \cdot \text{sec}^{-1}]$, where C is concentration in mol/liter, t is time in seconds.

Examples:

a) Photochemical reactions: $\text{H}_2 + \text{Cl}_2 \xrightarrow{h\nu} 2\text{HCl}$

The rate of the reaction depends upon quantum's of light

b) Hydrolysis of an ester:



The ester is taken in excess and its concentration will be constant because expense of the ester is constantly filled in from the ester layer. In this way the concentration of the aqueous layer will remain constant and the rate will not vary, $V = \text{const}$.

c) Decomposition of some compounds on the surface of different substances when the rate of decay doesn't depend on its concentration in volume.

2. First order Reactions.

Here the rate depends on the concentration. Kinetic equation is

$V = -\frac{dC}{dt} = k_1 C^1$, where k_1 is the rate constant. The unit of k_1 is sec^{-1} . $[k_1] = [\text{sec}^{-1}]$.

On separating the variables in equation $-\frac{dC}{C} = k_1 dt$ and integrating, we obtain $\ln C = -k_1 t + \text{const}_1$. Designating the initial concentration (of $t=0$) by C_0 , we determine the constant of integration $\text{const}_1 = \ln C_0$, whence

$$\ln C = -k_1 t + \ln C_0 \Rightarrow \ln C - \ln C_0 = -k_1 t \Rightarrow \ln \frac{C}{C_0} = -k_1 t; k_1 = \frac{1}{t} \ln \frac{C_0}{C}$$

or in common logarithm $k_1 = \frac{2,303}{t} \lg \frac{C_0}{C}$, where t is time; C_0 is the initial concentration; C is the concentration at t.

Examples:

a) Hydrolysis sucrose: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$

b) Decomposition of N_2O_5 : $2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$

c) Decay of radioactive elements

3. Second order reactions.

Kinetic equation is $V = -\frac{dC}{dt} = k_2C^2$ or $V = -\frac{dC}{dt} = k_2C_1C_2$, where k_2 is the rate constant.

The units of k_2 are therefore $\text{sec}^{-1} \cdot (\text{concentration}^{-1})$.

$$[k_2] = [\text{sec}^{-1}(\text{concentration}^{-1})] = [\text{liter} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}]$$

It should be noted that the rate constant for a second order reaction depends on the units of concentration used.

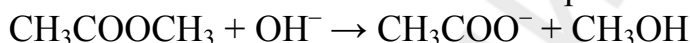
On separating the variables in equation $-\frac{dC}{dt} = k_2C^2$; $-\frac{dC}{C^2} = k_2dt$ and

integrating, we obtain $\frac{1}{C} = k_2t + \text{const}_2$. The constant of integration may be determined if the concentration C is known for a given time t . For instance if the initial concentration at $t = 0$ is known, then $\text{const}_2 = \frac{1}{C_0}$, whence $\frac{1}{C} - \frac{1}{C_0} = k_2t$,

or
$$k_2 = \frac{1}{t} \cdot \frac{C_0 - C}{C_0 \cdot C}$$

Examples:

a) Most well known second order reactions take place in solution



The «saponification» of an ester differs from first order aqueous hydrolysis in that the two reactants are present in approximately equal concentration, and both these concentrations affect the rate of reaction.

b) $2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$

c) $4\text{HBr} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Br}_2$.

The units of rates of different order reactions are equal and therefore we can compare them.

The reaction rate constants have different units and we cannot compare them. It may be compared the rate constants of chemical reactions if orders of reactions are equal.

4.5. Half – life of a reaction

The time in which half of the reactant is consumed is called the half-life of a reaction. It is the time in which the concentration of a reactant is reduced to one half of its initial concentration and is written as $t_{1/2}$.

1). Putting $t_{1/2}$ and $C = \frac{C_0}{2}$ into equation for the first order reaction we obtain

$$k_1 = \frac{2,303}{t} \lg \frac{C_0}{C} = \frac{2,303}{t_{1/2}} \lg \frac{C_0}{1/2C_0} = \frac{2,303}{t_{1/2}} \lg 2 = \frac{2,303 \cdot 0,3010}{t_{1/2}} \Rightarrow t_{1/2} = \frac{0,693}{k_1}$$

This equation shows that half-life for a first order reaction is independent of the initial concentration.

2). For a second order reaction the half-life is:

$$k_2 = \frac{1}{t_{1/2}} \frac{C_0 - 1/2C_0}{C_0 \cdot 1/2C_0} = \frac{1}{t_{1/2} \cdot C_0}, \text{ whence } t_{1/2} = \frac{1}{k_2 C_0}$$

This equation shows that half-life for a second order reaction depends on the initial concentration of the reactant.

The more $t_{1/2}$ the more substance is in the organism. This concept is important for toxicology and pharmacology.

For simple reactions powers in kinetic equations are the corresponding stoichiometric coefficients in chemical equation $aA + bB \rightleftharpoons cC + dD$ and $\frac{dC}{dt} = k[A]^a[B]^b$.

This regularity is in accordance with the Law of mass action which is formulated by Guldberg and Waage (1867).

The Law of mass action is a particular case of base postulate of chemical kinetics and is only applied for simple reactions.

The Law of mass action states that for a homogeneous system at constant temperature *the rate of simple reaction is directly proportional to the active masses of reactants in powers are the corresponding stoichiometric coefficients in chemical equation.*

4.6. Molecularity

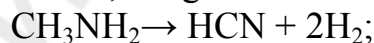
It is defined as the number of molecules colliding and leading to chemical transformations. Molecularity characterizes the simple reaction, i.e. elementary act of the reaction (individual steps by which a reaction proceeds).

Molecularity has a definite physical sense .

Classification of molecularity:

1. Unimolecular reactions.

To unimolecular reactions belong some molecular decompositions and intramolecular rearrangements. Thus, the gas reaction $I_2 = 2I$ is unimolecular;



For simple unimolecular reactions $V = kC$, where C is the concentration of the initial substance.

2. Bimolecular reactions.

Bimolecular reactions are those resulting from collision of two molecules of the same or different species: $CO + Cl_2 \rightleftharpoons COCl_2$; $I_2 + H_2 \rightleftharpoons 2HI$
 $V = kC_1C_2$, where C_1 and C_2 are the concentrations of the reactants.

3. Trimolecular reactions.

To trimolecular reactions belong those which require a collision between three molecules (of the same or different species) in order to take place. In the general case the equation for the rate of simple trimolecular reactions assumes the form $V = kC_1C_2C_3$; an example of such a reaction is $2NO + H_2 = N_2O + H_2O$.

Theoretically higher molecularities are possible, but actually the simultaneous collision of three molecules is already highly improbable and trimolecular reactions are encountered rarely. Practically no reactions of a higher molecularity are known.

Molecularity is always a whole number and never greater than three. A molecularity of four is not known because collision of four particles in a single step is not favourable.

When the equation of the reaction indicates that a large number of molecules participate, this usually means that the process must proceed in a more complicated manner, namely through two or more consecutive stages of which each is due to collision between two, or, rarely, three molecules.

For example, $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$. It is a complex reaction.

For simple reactions the order of reaction and molecularity coincides. For complex reactions the order of reaction and molecularity doesn't coincide more off.

Let's take another reaction: $\text{H}_2\text{O}_2 + 2\text{HI} \rightarrow \text{I}_2 + 2\text{H}_2\text{O}$.

The oxidation of iodide ions to iodine by hydrogen peroxide solution is known to proceed via the following mechanism:

First step $\text{H}_2\text{O}_2 + \text{HI} \rightarrow \text{HOI} + \text{H}_2\text{O}$ slow

Second step $\text{HIO} + \text{HI} \rightarrow \text{I}_2 + \text{H}_2\text{O}$ fast

General rate of this reaction is determined by the slowest step, which is called the rate controlling or rate determining step.

The *seeming molecularity* of this reaction is three. This reaction is complex; the order of this reaction is two. It is known, if molecularity and the order don't coincide, it means:

- 1) the reaction is complex,
- 2) the rate of this reaction is limited by rate determining step.

4.7. The effect of temperature on the rate of chemical reaction

Besides the concentrations of the reactants, the reaction rate must be influenced by the temperature, since raising the temperature increases the velocity of motion of the molecules, thus increasing the number of collisions. This dependence between the temperature and the reaction rate was first analyzed by Vant-Hoff (1887).

Vant Hoff's Rule: *each 10-degree rise in temperature approximately will speed up the reaction by 2–4 times.*

At temperature T the reaction rate is V_T at temperature $T+10$ the reaction rate is V_{T+10} then $V_{T+10}/V_T = \gamma$, where γ is *Vant Hoff's coefficient*.

From that equation we have: $V_{T+10} = V_T \cdot \gamma$ or in general $V_T = V_0 \gamma^{\Delta T/10}$.

The number characterizing the acceleration of a reaction due to raising the temperature 10°C is often called the temperature coefficient of the reaction or

Vant Hoff's coefficient. For most reactions the values of these coefficients under ordinary conditions lie between 2 and 4. As the temperature is raised, the coefficients decrease and gradually approach unity.

The γ shows how many times does the reaction rate increase for a rise in temperature of 10°C . But this dependence is very rough.

4.8. Collision theory

The collision theory gives more exact dependence (function) between temperature and the rate of reaction.

This theory is connected with Arrhenius (1889).

The rate of homogeneous reactions depends on a number of collisions of the reacting particles per unit time. The number of collisions, in turn, is directly proportional to the concentration of the reactants.

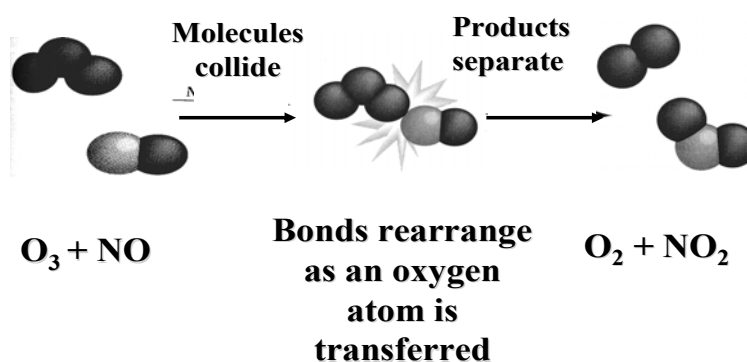


Fig. 4.3. The reaction between ozone and NO is believed to occur by a mechanism that consists of the single bimolecular step shown here in a molecular view

The collision theory is built on a number of assumptions.

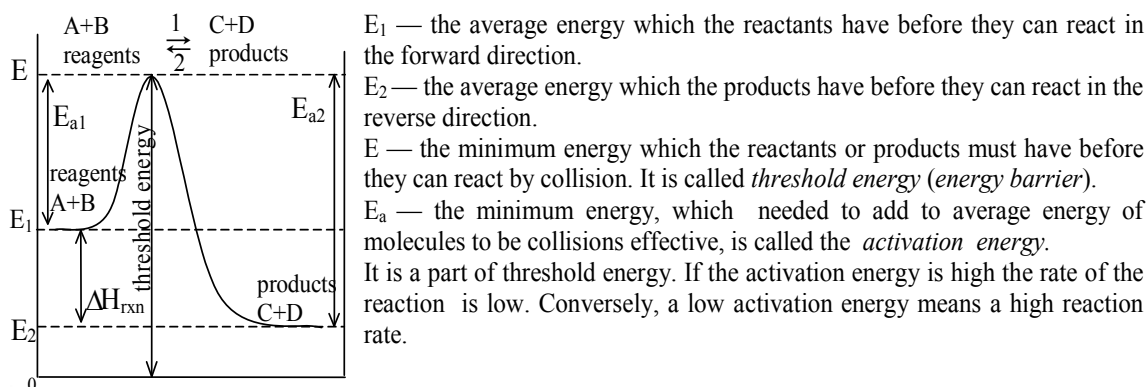
1. A chemical reaction takes place when collisions take place between the reacting particles: atoms, molecules or ions.
2. No each collision between reactants is effective; effective in the sense that a reaction occurs.

According to the collision theory that only those collisions which involve more than a certain amount of energy, result in the formation of products. Obviously, not all collisions between reactants can lead to a reaction (fig. 4.2).

Energetic diagram (fig. 4.4) shows a rate of chemical reaction (elementary step of the reaction).

Reaction coordinate is a function of distance between atoms.

The term «reaction coordinate» refers to the relative distance between particles involved in the reaction. An average kinetic energy doesn't enough for overcoming of threshold energy.



E_{a1} — the activation energy of forward reaction (1). E_{a2} — the activation energy of reverse reaction (2).

$E_{a1} < E_{a2}$

ΔH_{rxn} — is the heat effect of a reaction. According to the graph of fig. 4.1, ΔH of forward reaction (1) is negative ($\Delta H < 0$). In other words this reaction is exothermic ($E_1 > E_2$). ΔH of reverse reaction (2) is positive ($\Delta H > 0$), i. e. an endothermic reaction ($E_2 < E_1$).

Fig. 4.4. Energetic diagram

Normally, only a small fraction of the reacting molecules have enough kinetic energy to exceed the activation energy. The higher the temperature the greater the kinetic energy of reacting molecules and the larger is a fraction of active molecules in a mixture. Thus increase in temperature accelerates most chemical reactions.

According with Arrhenius the fraction of active collisions from total numbers of collisions is denoted as α and equals $\alpha = e^{-E_a/RT} = Z/Z_0$, where e is the base of natural logarithm; Z_0 is the total number of collisions; Z is the number of active collisions; E_a is the energy of activation [$J \cdot mol^{-1}$]; R is the molar gas constant equal to $8.314 J/mol K$; T is absolute temperature.

From expression Z (the number of active collisions) can be obtained:

$$Z = Z_0 e^{-E_a/RT}, \text{ where } \alpha = e^{-E_a/RT}$$

If a large-sized molecules react (proteins) it should be taken into account the steric factor \mathbf{P} . It is known that collisions even between active molecules do not always result in a reaction. The molecules must have a definite orientation. The proteins have active groups and macromolecules of proteins must have a definite orientation to collide their active groups.

The steric factor \mathbf{P} takes into account a definite orientation or a favourable spatial collision.

The factor \mathbf{P} is proportional to the ratio of the number of ways of the mutual orientation of the molecules favourable for proceeding of a reaction to the total number of possible ways of orientation: the greater this ratio the more rapidly will a reaction proceed. The steric factor \mathbf{P} is usually much smaller than unity; it has an especially great influence on the rate of reactions proceeding with the participation of complex molecules (for example proteins), when the total number of various possible orientations is very great, and the number of favourable orientations are very limited:

$$Z = Z_0 \cdot P \cdot e^{-E_a/RT}$$

Arrhenius suggested the equation: $k = A \cdot \alpha$, $k = A \cdot e^{-E_a/RT}$, where k is rate constant; A is the total numbers of double collisions per second in 1cm^3 of reaction system, A is a constant known as Arrhenius or frequency factor or A is a constant preexponential factor independent of the temperature and concentration; $\alpha = e^{-E_a/RT}$ is exponential factor, it is called Boltzmann factor and gives the fraction of collisions with energies greater or equal to activation energy.

Two important conclusions can be drawn from the Arrhenius equation:

a) at constant temperature the greater the activation energy, the slower is the reaction;

b) as temperature increases, rate of reaction also increases.

As the rate constant k is a product of two multipliers A and $e^{-E_a/RT}$ the k is a measure of the number of activated molecules per unit volume or *it has a sense of the number of active collisions*.

The temperature generally affects the exponential factor to a greater extent than the preexponential one. It is explained that the elevation of the reaction rate with increasing of temperature only depends on increasing the fraction of active collisions from total number of collisions. The higher temperature T , the less E_a/RT and the higher $A \cdot 1/e^{E_a/RT}$.

The following conclusions can be drawn from equation $k = A \cdot e^{-E_a/RT}$:

1. Even a slight decrease in the activation energy increases the rate of reaction quite substantially.

2. The temperature generally affects the reaction rate to a greater extent when the activation energy of a reaction is higher.

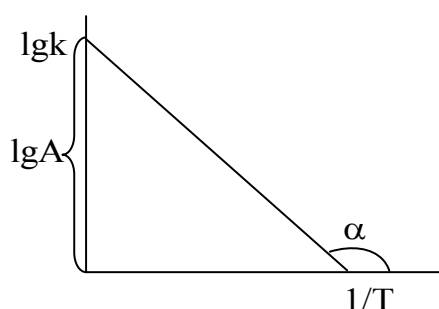
3. Reactions with high activation energies proceed at low rates when the temperature is low, but the influence of the temperature on the rate of such reactions is usually more appreciable (the temperature coefficient γ is larger).

The Arrhenius equation shows that the rate constant of a reaction grows with a decreasing activation energy.

Calculation of Activation energies from the Arrhenius equation. Let us see how equation $k = A \cdot e^{-E_a/RT}$ is applied for determining the activation energy. This equation is considerably simplified if the logarithm of the rate constant is taken as a function of the reciprocal absolute temperature:

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \quad \text{or} \quad \lg k = \lg A - \frac{E_a}{2,3R} \cdot \frac{1}{T}$$

Calculate the rate constant for different temperatures.



The experimental data $\frac{1}{T}$ and $\lg k$ usually give a straight line (fig. 4.5).

Fig. 4.5. The relationship between $\lg k$ and $1/T$

Hence the logarithm of the rate constant of a reaction is practically linearly related to the reciprocal temperature ($1/T$):

$$\lg k = -\frac{E_a}{2.3R} \cdot \frac{1}{T} + \lg A; \quad E_a = -2.3R \cdot \text{tg} \alpha \text{ at } 1/T = 0; \quad \lg k = \lg A.$$

The collision theory gave an idea about active collisions and activation energy, proposed calculations for many reactions, but this theory is not free from limitations.

First of all the collision theory didn't explain the mechanism of the collision.

The collision theory doesn't explain reaction's mechanism, influence of a solvent and other factors on the rate of a reaction.

The collision theory only states that reaction can proceed after active collision from total number of collisions.

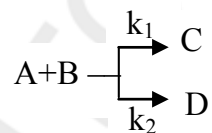
4.9. Concept about kinetics of complex reactions

Most reactions are complex.

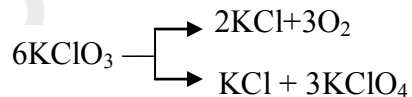
The kinetics of complex reactions consisting of simple reactions, connected in one way or another, depends upon the nature of their interrelation and on the ratio of their reaction rates. Typical forms of such interrelations are: *simultaneous*, *consecutive*, *conjugate*, *reversible* reactions.

The theory of these reactions is based on the principle that when several reactions occur simultaneously, each takes place independently and each obeys the kinetic equations of the simple reactions.

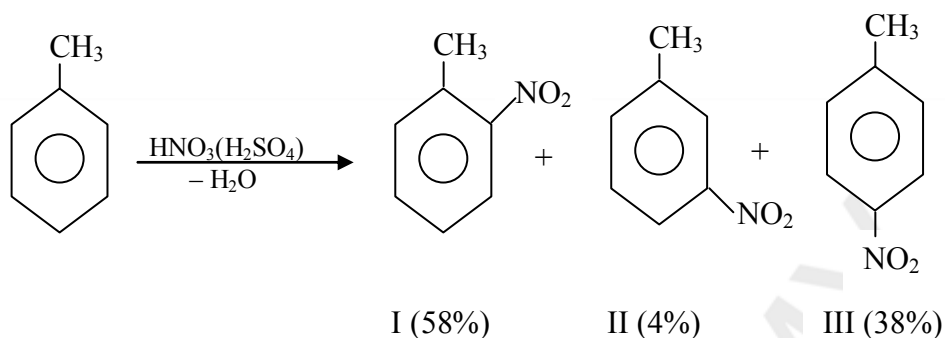
1. *Simultaneous reactions* are those of the type



In such reactions the initial substance or substances can react simultaneously in different directions. An example of parallel reactions is the decomposition of potassium chlorate, which at moderate temperatures may occur in two parallel directions:



The other reaction is nitration of toluene. This reaction is the first stage for manufacture of novocain.



Toluene reacts with a mixture of concentrated nitric and sulphuric acids. The first product is a mixture of ortho- and para-nitro toluene (I,III). The latter product is very important for manufacture of anesthetic.

Simultaneous reactions are most frequently encountered in organic chemistry. For instance in the nitration of toluene with nitric acid in the presence of concentrated sulphuric acid the nitro group may occupy either the meta-, ortho- or the para-position (II, I, III).

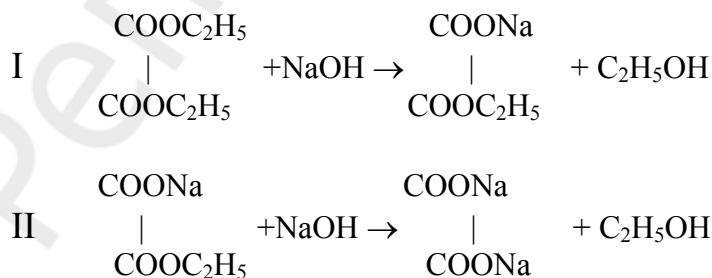
If the reactions differ considerably in rate the reaction with the highest rate is usually called the *main reaction* and the others *side reactions*. However, if the difference is not very great, the main reaction is considered to be that which leads to the desired product, although its rate may be lower.

2. *Consecutive reactions* are those of the type $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where B is an intermediate in the formation of C, and k_1 and k_2 are the rate constants of the two stages of the reaction.

Scheme is that for the simplest type of consecutive reactions. It occurs in two stages, each of which is a simple unimolecular reaction. In the general case the number of stages may be more than two, and the stages may be not unimolecular.

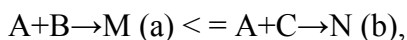
Consecutive reactions are very wide spread. Among them is hydrolysis of dicarboxylic acid esters of glycol esters or of diacyl chlorides. The kinetics of consecutive radioactive transformations may be considered as a particular case of the kinetics of a series of consecutive first order reactions.

A simple illustration of consecutive reactions may serve the saponification of diethyl oxalate by sodium hydroxide, which proceeds in two consecutive stages:



Calculation of the rates of consecutive reactions in the general form is very complicated. We shall only point out that *if one of the stages proceeds at a considerably lower rate than all others the over-all rate of the reaction will be determined by the rate of this stage.*

3. *Conjugated reactions* are defined as reactions of the type:



of which one, for example (a), takes place only together with the other, i.e. induced by the other (b). In such cases the substance C is an initiator for the first reaction. An example of such reactions are: hydrolysis of ATP (b) and the synthesis of proteins and peptides (a) in the living organism.

The free energy released by hydrolysis of ATP is necessary for the synthesis of proteins and peptides in living organism.

$\Delta G < 0$ hydrolysis of ATP — exergonic reaction;

$\Delta G > 0$ formation of peptide bond — endergonic reaction.

4. *Reversible reactions*

Reversible reactions proceed under given conditions both in the forward and reverse directions simultaneously $A+B \xrightleftharpoons[k_2]{k_1} C+D$, where k_1 is the rate constant of forward reaction; k_2 is the rate constant of the reverse reaction.

The state of a system when the rates of the forward and reverse reactions are equal: $V_1 = V_2$; $k_1 C(A)C(B) = k_2 C(C)C(D)$ is called a state of chemical equilibrium.

It is readily seen that on reaching a state of chemical equilibrium the concentration of each component of the reaction will remain constant.

Chemical equilibrium is dynamic, i. e. its setting in does not mean that the reaction has stopped.

Chemical equilibrium is characterized quantitatively by a quantity known as the *chemical equilibrium constant*.

The chemical equilibrium constant is the ratio of the rate constant of the forward and reverse reactions: $\frac{k_1}{k_2} = \frac{C(C)C(D)}{C(A)C(B)} = K_c$, where K_c is the chemical equilibrium constant expressed in terms of the equilibrium concentrations of the reactants and products.

The equilibrium constant determines the extent of a process by the instant of reaching the equilibrium state. The larger this quantity, the greater is degree of conversion of the reactants into the products.

The equilibrium constant depends on nature of the reactants and the temperature.

5. *Chain reactions*. Up to now, we dealt with chemical reactions proceeding comparatively simply. There is a broad group of reactions, however, that proceed in a more complicated way. Here, the formation of macroscopic

amounts of the product is the result of a chain of elementary events of interaction. Such reactions are known as chain ones.

Chain reactions proceed with the participation of *active centers* – atoms, ions or radicals (fragments of molecules) having unpaired electrons and displaying, as a result, a very high reactivity.

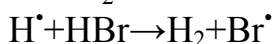
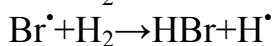
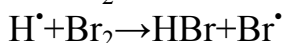
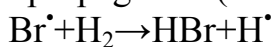
The active centers are the initiators of chains of consecutive transformations of substances.

A simple example of a chain reaction is the reaction between gaseous bromine and hydrogen expressed by the ordinary equation: $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$.

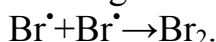
The chain reactions consist of some steps.

The first step – the initiation of the chain. Bromine molecules dissociate and this process can be expressed by the equation: $\text{Br}_2 \rightarrow \text{Br}^\cdot + \text{Br}^\cdot$.

The second step the propagation (and branching) of the chain



The third step the breaking of the chain (or the termination of the chain):



The same mechanism can prevail for the reaction between hydrogen and chlorine, oxidation of hydrocarbons, burning, explosions, polymerization reactions.

This is why the theory of chain reactions is the scientific foundation of a number of important branches of engineering and chemical technology.

Radical reactions proceed in vivo under the affect of different free radicals OH^\cdot , HOO^\cdot , ROO^\cdot , O_2^\cdot and some other. Scientists came to the belief that accumulation of free radicals in intracellular fluids is one reason for aging.

Rate of radical reactions can be increased greatly under the influence of radiation. Even small dozes of radiation can accelerate generation of free radicals. Free radicals cause the destruction of cell membranes, suppress immune system of people, and cause different diseases. Radical reactions can be retarded by antioxidant substances: vitamins A, E, C and Selenium compounds.

Chains reactions also include nuclear chain reactions proceeding in atomic reactor or upon the explosion of an atomic bomb.

6. *Photochemical Reactions.* Photochemical reactions are reactions that take place under the influence of light (visible light, ultra-violet) or more seldom, infrared rays. Such reactions can occur in gases, liquids and solids. Molecules of reacting substances are excited by absorbing quanta of light under the photochemical effect of light, i.e. become reactive or decompose into ions and free radicals.

The photochemical reactions are characterized by quantum output (γ).

$$\gamma = \frac{\text{(an amount) a number of molecules of products}}{\text{an amount of absorbed quanta}}$$

The most important photochemical reaction is undoubtedly the photosynthesis taking place in plants. For example the reaction $6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ occurs in the presence of light. Under the action of solar light chlorophyll converts the CO_2 of the air into complex molecules of organic substances. In this case the light energy transforms into the energy of chemical bonds. This process is endothermal, taking place with increase in the Gibbs free energy ($\Delta G > 0$). It cannot occur in the absence of light.

Photochemical reactions are highly varied. Among them are the photosynthesis of carbohydrates carried out by plants under the action of the sun's rays, the photographic processes, luminescence phenomena, decolourization of dyes, etc. Photochemical reactions also greatly differ chemically. Under the action of light synthesis (phosgene, hydrogen chloride), decomposition (hydrogen peroxide), oxidation, etc. may take place.

The photochemical reactions are applied in medicine – the oxidation of bilirubin at jaundice of premature babies, the photochemical processes underlie mechanism of vision.

4.10. Catalysis and catalysts

Substances that are not consumed in a reaction, but affect its rate, are called *catalysts*. The phenomenon of the change in the rate of a reaction under the action of such substances is known as *catalysis*. Reactions proceeding under the action of catalysts are called *catalytic*.

The action of a catalyst in the majority of cases is explained by the fact that it lowers or increases the activation energy of a reaction. The catalyst is called *negative*, when it increases the activation energy; the catalyst is called *positive*, when it lowers the activation energy (table 4.1).

In the presence of a catalyst a reaction proceed through other intermediate stages than without it, and these stages are more accessible from the energy viewpoint.

Table 4.1

Activation energy of catalytical and noncatalytical chemical reactions

Reactions	E_m kJ/mol		Catalyst
	without a catalyst	with a catalyst	
$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	180	40	Pt
		8	Cu
$2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	750	55	I_2

The catalyst doesn't effect on the total number of collisions in practice but has effect on the activation energy.

Catalyst have no effect on chemical equilibrium since they equally accelerate or lower the direct or reverse reactions. Catalysts only accelerate or lower

the establishment of equilibrium in the system. *Catalysts have no effect on the equilibrium constant (K_c).*

Depending on the physical state of the catalyst and reacting substances, *homogeneous and heterogeneous catalyses* are distinguished.

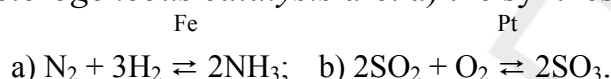
Examples of a *homogeneous catalysis* are:

a) the oxidation of CO (in the gaseous state in the presence of water vapour) by oxygen $2\text{CO} + \text{O}_2 \xrightarrow{\text{H}_2\text{O}} 2\text{CO}_2$;

b) $2\text{SO}_2 + \text{O}_2 \xrightarrow{\text{NO}} 2\text{SO}_3$;

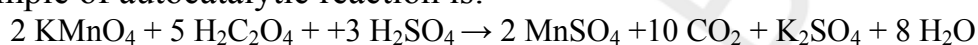
c) the action of various enzymes in biological processes.

Examples of a *heterogeneous catalysis* are: a) the synthesis of ammonia



Autocatalysis is a process when a product of a reaction acts as a catalyst.

An example of autocatalytic reaction is:



Catalyst: Mn^{2+}

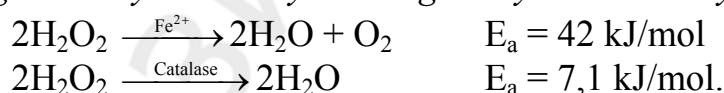
Catalysts are used very broadly in the chemical industry.

4.11. Enzymes

Catalysis plays a very great role in biological systems. Most chemical reactions proceeding in the digestive system, in the blood and cells of animals and man are catalytic reactions. The catalysts, which in this case are known as enzymes, are simple or complex proteins. Thus, saliva contains enzyme ptyalin, which catalyzes the transformation of starch into sugar. An enzyme in the stomach, pepsin, catalyzes the decomposition of proteins. The human organism contains about 30000 various enzymes; each of them is an effective catalyst of the corresponding reaction.

Distinctive traits (properties) of enzymes:

1. *High catalytic activity. The high enzymatic activity.*



In the presence of the enzyme catalase (found, in particular, in the erythrocytes), this reaction can be effected at a much greater rate, yielding the same end products of hydrogen peroxide breakdown. Hydrolysis urea: by acid $E_a = 103 \text{ kJ/mol}$; by enzyme urease $E_a = 28 \text{ kJ/mol}$.

2. *Highly specific to substrate. High enzymatic specificity to substrate. High selectivity (one enzyme activates only one or two biochemical reactions).*

Enzymes exhibit specificity of action. In many instances, this property is the essential characteristic.

For example, pepsin splits the proteins of animal and vegetal origin but doesn't split carbohydrates or fats. Amylase splits starch, but doesn't split a saccharose although they are built of glucose residues.

3. *Enzymes act under mild conditions*: body temperature 25°–40 °C; normal pressure.

4. *Enzymatic reactions proceed without side reactions (side effects)*.

5. *The rate of any enzymatic reaction depends on the enzyme and substrate concentrations*. The greater the enzyme concentration the greater the rate of enzymatic reaction. i. e. the reaction rate is proportional to the concentration of the enzyme present. The enzymatic reaction rate is proportional to the substrate concentration too.

At low substrate concentrations the reaction rate is directly proportional to the substrate concentration $V = k_1C$ and obeys the first order kinetics. At high substrate concentrations, the reaction rate attains a maximum and becomes constant, independent of the substrate concentration $[S]$. In this instance, the reaction obeys the zero order kinetics: $V = V_{\max} = k_0$ (as the enzyme becomes fully saturated with substrate) and is wholly determined by the concentration of enzyme (fig.4.5).

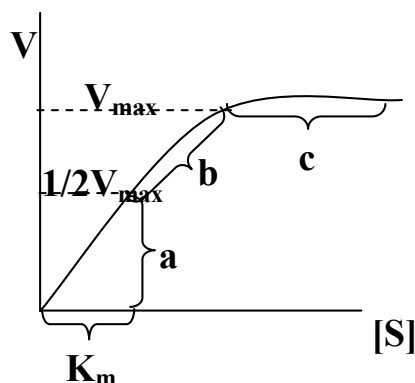


Fig.4.5. Theoretical relationship between the enzymatic reaction rate (V) and the substrate concentration [S] at a constant concentration of the enzyme

- a) first order reaction (of $[S] > K_m$, the reaction rate is proportional to the substrate concentration);
- b) mixed order reaction;
- c) zero order reaction ($V = V_{\max}$, and the reaction rate is independent of the substrate concentration).

In their studies on enzyme saturation effect, L. Michaelis and M. Menten have developed a general theory of enzymatic kinetics.

They proposed the following chemical reaction $E + S \xrightleftharpoons[k_2]{k_1} [ES] \xrightarrow{k_3} E + P$, i. e. the enzyme E reacts with the substrate S to form an intermediate complex [ES] which further dissociates into a free enzyme and the reaction product P.

V_{\max} is the maximum rate of reaction for complete saturation of enzyme with substrate.

The substrate concentration of which enzymatic reaction rate V is half the maximum rate i. e. $V = 1/2V_{\max}$ is called by the *Michaelis constant* K_m .

K_m characterizes stability of enzyme-substrate complexes. The lower is K_m , the higher stability of a complex.

Factors affecting enzymatic reactions are:

1. *Temperature*
2. *Acidity and basicity of medium*
3. *Enzyme inhibitors.*

Enzymes work best at an optimum pH value, which varies from enzyme to enzyme. Most enzymes that are active within cells have a pH optimum fairly close to the range of pH within which cells normally function (fig.4.6). For example, the pH optima of two digestive enzymes, pepsin and trypsin, occur at about pH 2 and pH 8 respectively.

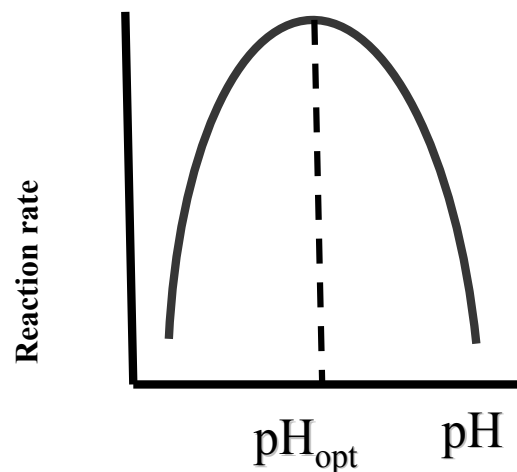


Fig. 4.6. The effect of acidity on enzymes' activity

We will consider two forms of inhibition (there are others):

1. *Competitive inhibition* (fig.4.7).
2. *Noncompetitive inhibition* (fig.4.8)

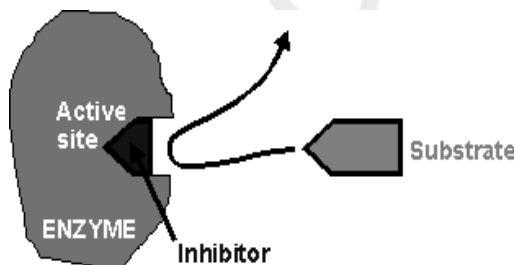


Fig. 4.7. Competitive inhibitors generally structurally similar to substrate and bind to active site – keeping out the substrate

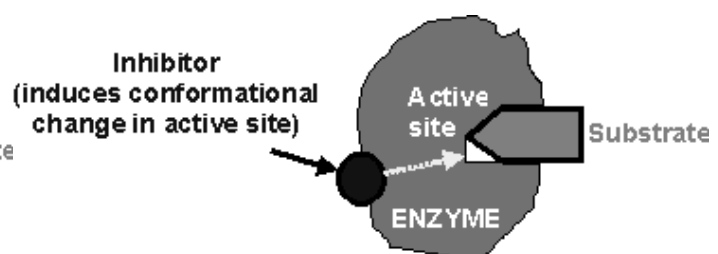


Fig. 4.8. Noncompetitive inhibitors bind away from the catalytic site but cause a conformational change to be transmitted to the active site

Practical application of Enzymes. Enzymes find wide application in many branches of food industry such as bread baking, brewing, wine production, tea production, tanning and fur dressing, cheese industry, cookery (in preparatory treatment of meat), etc. In recent years, enzymes are being increasingly used in chemical industry for carrying out chemical reactions such as oxidation, reduction deamination, decarbonylation, dehydration, and condensation as well as for resolving and separating α -amino acid isomers for use in industry, agriculture and medicine.

At present, a new branch of knowledge, the industrial enzymology, is emerging, laying down the basis for further advance in biotechnology. An enzyme covalently bound («grafted») to an organic or inorganic carrier is called the *immobilized enzyme*. The technique of enzyme immobilization opens a route to the solution of key problems in enzymology including the provision for high specificity of enzymes and improvement to their stability, the ease of utilization and the feasibility of repeated use and application to flow processes of chemical synthesis. The industrial applications of such enzyme based techniques have become known as the *engineering enzymology*.

The immobilized β -galactosidase is used as means to decrease the milk sugar content in milk, which helps in dealing with the problem of lactose intolerance. Moreover, the milk thus processed can be stored in a frozen state for a longer period of time without souring.

Cellulose can be converted to glucose through the use of immobilized cellulases. In principle, the engineering enzymology can provide a means for obtaining alimentary products, in particular, carbohydrates, from liquid fuel (petrol) by splitting it to glyceraldehyde and then proceeding, with the participation of enzymes, to the synthesis of glucose and starch.

The progress in enzymology is increasingly gaining ground in medicine, especially, in many aspects of prophylaxis, diagnosis, and therapy. A notable progress has been recorded in a novel branch of enzymology — *medical enzymology*.

Medical enzymology is now advancing in three major directions.

1. *Enzymopathology*, which is concerned with the investigation of enzymatic activity in norm and pathology. As has been ascertained many hereditary disturbances of metabolism originate in the defect of a definite enzyme. For example a hereditary disease, phenylketonuria, manifested by neurologic disturbances, is the lost capacity of the liver cells to synthesize the enzyme that catalyzes the conversion of phenylalanine to tyrosine.

2. The second trend is *enzymodiagnosics* which is concerned with both the use of enzymes as selective reagents for identification and quantization of

normal and abnormal chemical substances in blood plasma, urine, gastric juice (for example, for enzymatic urinary analyses of glucose, proteins and other substances, not detectable when they are in norm in urine, and the qualitative and quantitative analyses of the enzymes themselves in biological fluids under pathology. It should be remembered, however, that out of the whole wealth of enzymes (over 2000) that have been discovered in nature (and, partly, in the human organism), the diagnostic enzymology makes use of a rather limited set of enzymes and besides, for the diagnosis of a still smaller number of diseases (hepatitides, myocardial infarction, organic damage of the liver and others). Thus, the level of lipase, amylase, trypsin and chymotrypsin becomes drastically elevated in diabetes, malignancy of the pancreas, hepatic diseases, and other states.

3. The third trend in medical enzymology – *enzymotherapy*, i. e. the use of enzymes and regulators of enzymatic activity.

In the clinic, pepsin, trypsin and mixtures there of are used to treat the gastrointestinal tract. RNase, DNase, hyaluronidase, collagenases, elastases taken separately or in combination with proteins, are used for the treatment of wounds, skin burns, and for the removal of edemas, hematomas, keloid cicatrices (in pulmonary tuberculosis). Enzymes are also applied in the treatment of cardiovascular diseases and for the dissolution of blood clots, for these purpose the immobilized streptokinase has been obtained.

CHAPTER 5 SOLUTIONS AND THEIR PROPERTIES

5.1. Thermodynamics of the process of solution formation

A solution is a homogeneous system consisting of two or more components the relative quantities of which may vary over a fairly wide range.

The most important are liquid solutions, which will be considered in this guide.

Any solution consists of a dissolved substance called the solute and the medium in which the solute is uniformly distributed as molecules or ions, called the solvent.

A solvent is a component that determines the state of a solution. It is usual to think of the component present in the largest amount as the solvent and the other component(s) as the solute. Solvents can be polar (H_2O , concentrated H_2SO_4) and non-polar (benzene, acetone, alcohols).

Water is the most important solvent in nature and the most abundant substance in the world. The unique physicochemical properties of water are responsible for its numerous biological functions in a human body. Water has one of the highest polarities of all liquids. This property makes water an excellent solvent for ionic compounds. Due to its very high heat capacity water regulates temperature of a cell from the heat generated by metabolic processes; due to its high molar heat of vaporization water protects a human body from overheating.

The human body is made mainly of water ($\frac{2}{3}$ of the body mass). Different organs and tissues contain variable amount of water: **b**rain contains 75 % of water and even moderate dehydration or lack of water can cause headaches and dizziness; **h**ear**t** and **m**uscles — 75 % of water; **b**ones — 22 % of water; **l**ungs and **l**iver — 86 % of water; **k**idneys and **b**lood — 83 % of water.

The loss of $\frac{2}{3}$ volume of intra-cellular fluid may cause death. The excess of water is also dangerous; it may result in cell swelling and edema.

The process of solution formation is a spontaneous process. When a solute is dissolved in a solvent, we mean that the attractive forces between solute and solvent particles are great enough to overcome the attractive forces within the pure solute and solvent. When solutes are dissolved, they become solvated if solvent molecules are bonded firmly to solute molecules or ions. If water is the solvent, this is called more specifically hydration.

Solubility is the maximum amount of material that will dissolve in a given amount of solvent at a given temperature to produce a stable solution. According to the solubility amount the solutes are divided into soluble, insoluble and low-soluble.

If two liquids mix to a considerable degree to form a solution they are said to be mixable. In contrast, immiscible liquids will not mix to form a solution; they will exist in contact with each other as separate layers. The nonpolar

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