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C51 **CHEMISTRY, Grade 10:** Textbook / Kanat Baikenov, Temirlan Khassen,
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PREFACE

Natural science is an exciting and very useful subject. This textbook will show you all the beauty of it and will help you become true explorers. The main aim of this book is to answer the fundamental question: "What is science and what is its importance in our life?"

Starting from the first pages, you will realize that this textbook is completely different from any other usual textbook full of theoretical passages and formulas. Every chapter contains useful information, curious facts, tasks for individual and group work. You will also learn how to conduct research and experiments yourselves, search for information, make your own discoveries.

One more valuable feature of this textbook is the language. Every sentence has been carefully chosen so that it is not difficult for you to understand science in English language. Each page contains the translation of all the important terms, both in Kazakh and Russian. This textbook will not only help you improve your English, but it will also make you a part of a big international science community.

Please pay attention to the structure of this textbook. Remember: a textbook is no longer the only source of information in a modern world. With the help of carefully selected tasks, you are going to learn such important skills as critical thinking, problem solving, information analysis, creativity, imagination, teamwork, digital literacy etc.

If you have any questions, suggestions or ideas regarding the contents of this book, please feel free to contact us:

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- via telegram app:	@astanakitap

Best regards,,
team of authors, "Astana-kitap"

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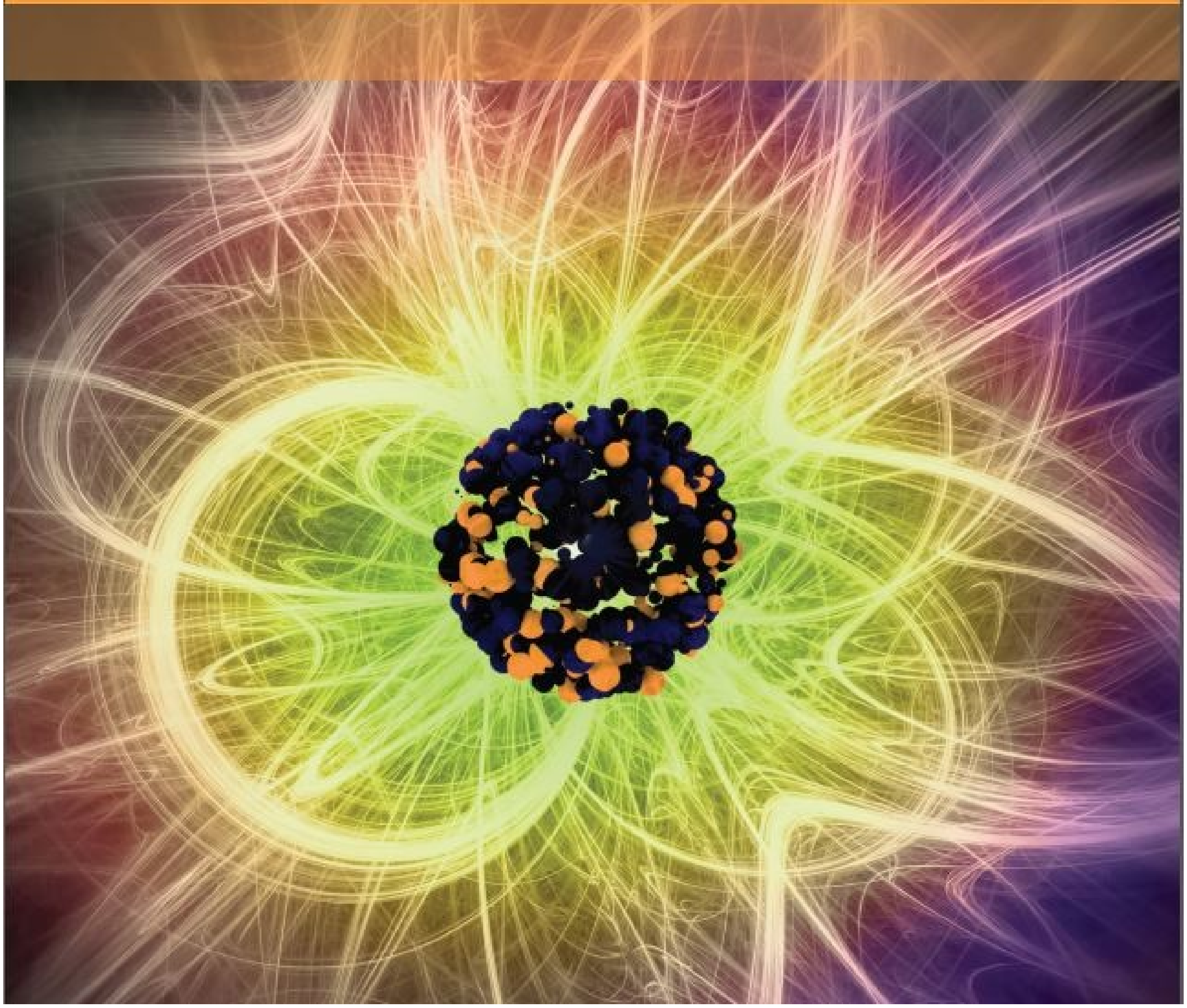
STRUCTURE OF AN ATOM



CHAPTER 1: STRUCTURE OF AN ATOM

1.1 ATOM. AVERAGE RELATIVE ATOMIC MASS

Atomic mass of an atom is equal to a total number of protons and neutrons. For example, if an atom has 8 protons and 8 electrons its mass is roughly 16 amu. Why are the atomic masses of elements given as fractional numbers in the periodic table?

You will:

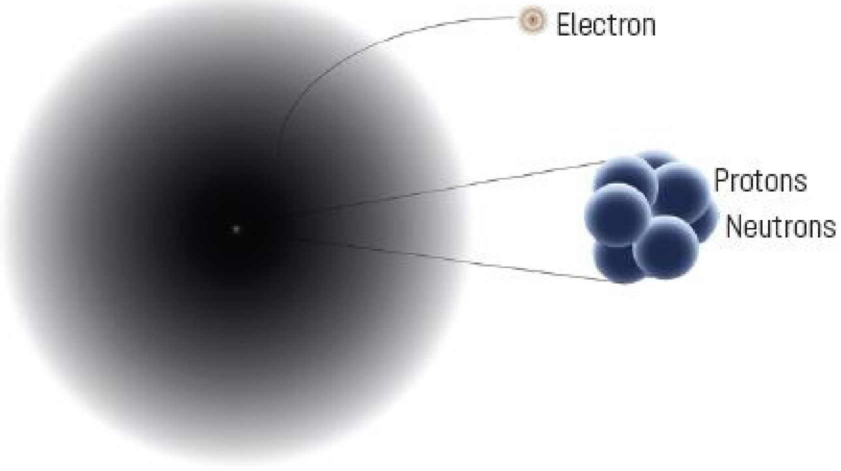
- understand the concept of isotopes and nuclides;
- solve average relative atomic mass of a mixture of isotopes.

Atoms consist of three subatomic particles, namely proton, electron and neutron. Protons and neutrons are located in the centre of an atom, and they are collectively called a nucleus. Electrons are located around the nucleus in the form of electron clouds. Proton number or atomic number is designated by a letter “Z” (or “p”), and neutron number by “n”. Protons are positively charged, electrons are negatively charged, and neutrons are neutral species. The volume of a nucleus compared to the atom itself is very small. If we enlarge an atom’s size as large as the pavilion “Nur Alem”, then the nucleus would be smaller than a tip of a pen.

Pen tip

"Nur Alem" Pavilion in Astana

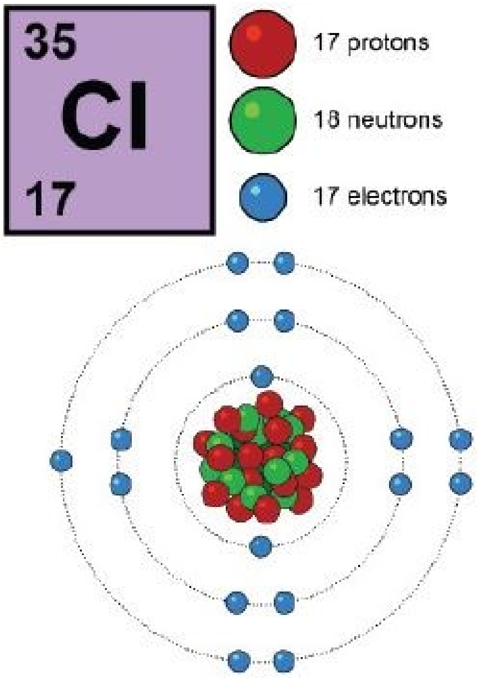
Some atoms can have the same number of protons, but different atomic mass. These types of atoms are called isotopes. If we have a group of atoms, which have the same number of protons, then we surely can say that the group is composed of only one type of element. For instance, if we have a 100 g sample of an element with proton number of 17, then we can say that all atoms in that sample are chlorine atoms. However, if we have 100 grams of a purified sample of naturally occurring chlorine, then it is composed of two different types of atoms or nuclides (but both are chlorine), that is to say, 75.78 grams of ^{35}Cl, and 24.22 grams of ^{37}Cl. Although they are different, as their masses are different, they are isotopes. Similarly, chlorine in table salt consists of 75.78% ^{35}Cl, 24.22% ^{37}Cl isotopes. Virtually all elements in nature have isotopes; however, there are some, like aluminium, which naturally exists as a single nuclide ^{27}Al.

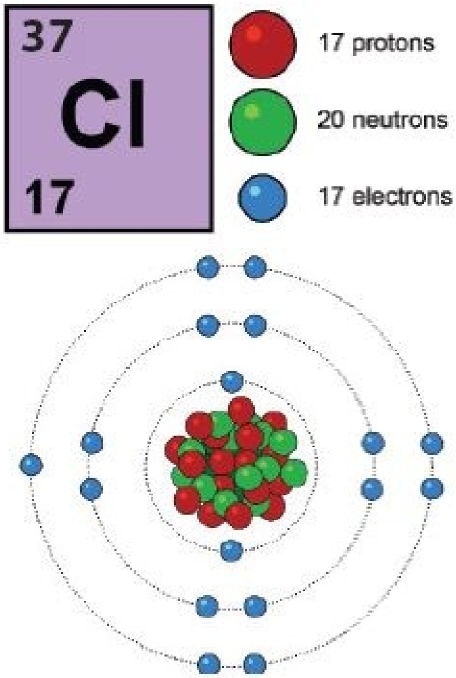


Atom and subatomic particles

In order to find the average atomic mass of an element, we have to take into account the abundances of the natural isotopes of that element.

$$\text{Average atomic mass} = \frac{(\text{\% of isotope 1} \times \text{mass of isotope 1}) + (\text{\% of isotope n} \times \text{mass of isotope n})}{100}$$





Keep in mind:

Nuclides are an atom or ion characterized by the contents of their nucleus.

Research time

Open in browser The scale of the Universe (htwins). Research about subatomic particles.

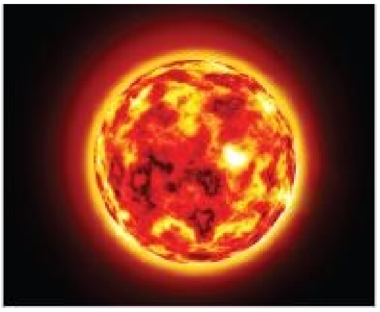
Research time

Open in browser Phet. Rutherford Scattering.
In Rutherford's scattering experiment, why is the alphaparticle not affected by the negative charge present in the Gold foil?
What is the path traveled by alpha particles in the Rutherford scattering experiment?

Chemfact

What are the reactions inside the Sun?

Two isotopes of hydrogen (deuterium and tritium) collide with each other to give helium isotope and free neutron (heat and radiation rays)



Example

Calculate the average atomic mass of chlorine, if the abundances of isotopes are 75.78% of 35Cl and 24.22% of 37Cl.

Solution

By using the above formula, we can find that:

$Ar(Cl)=[(75.78 \cdot 35) + (24.22 \cdot 37)] / 100 = 35.5$

Literacy

1. Three elements are given. You know only neutron number of first, atomic mass of second, and proton number of third element. Which of these elements can you identify? Explain why.

2. Calculate the average atomic mass of copper, if the abundances of isotopes 63Cu and 65Cu are 69.17% and 30.83%, respectively.

3. Gallium has two natural isotopes 69Ga and 71Ga. If the average atomic mass of gallium is ~69.798, calculate the abundances (in %) of these two isotopes.

4. Is it possible for an element to exist without a neutron? How

about a proton?

5. Calculate the average atomic mass of iron, if the abundances of isotopes are 5.845% of 54Fe, 91.754% of 56Fe, 2.119% of 57Fe and 0.282% of 58Fe.

Chemistry around us

Tritium (3H) isotope used in self-powered lighting devices such as “exit signs”, watches and map lights.

Chemfact

The element astatine, which was not discovered until the 1940’s, was first named eka-iodine. All 21 isotopes of astatine are radioactive, and it is virtually non-existent in nature (only approx. 30 g). However, it can be artificially synthesized in trace amount by bombarding the nuclei of bismuth with (α) particles.

Terminology

- to designate - белгілену / обозначать;
- to omit - есепке алмау / пропускать

1.2 RADIOACTIVITY

What are the advantages and disadvantages of nuclear energy in our world?

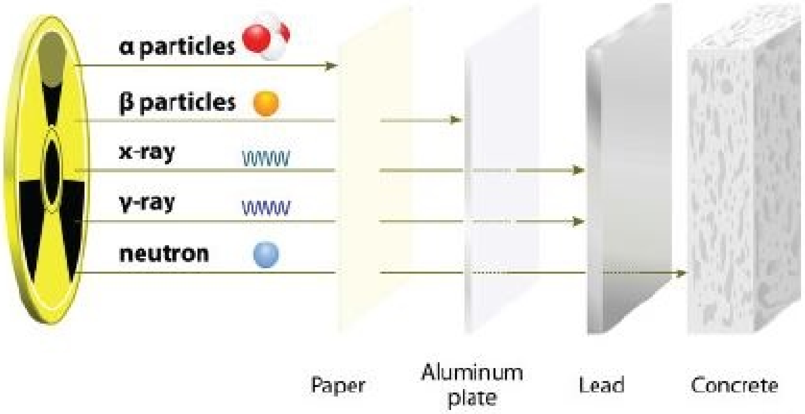
You will:

- explain nature of radioactivity and application of radioactive isotopes;
- use proton-neutron ratio for identifying the stability of isotopes;
- write equations for nuclear reactions.

You already know that atoms consist of three subatomic particles. Protons and neutrons, which are collectively called nucleons make up the nucleus. Electrons are “rotating” around the nucleus and nucleus’ positive charge holds them due to the electromagnetic force.

You can think of neutrons as particles which play a key role in holding protons in such a tiny nucleus. If there were no neutrons, it would be impossible to hold positively charged protons in a small nucleus. That is why as the mass of atoms increase, more neutrons are needed to hold positively charged protons.

The force that holds protons and neutrons in a nucleus is called a strong force. It is much stronger than the electrostatic force for about ~140 times. However, the strong force functions over the very small distances. That is the reason why nuclei of elements such as uranium and bohrium are unstable. As strong force operates on small distances, and above mentioned elements’ nuclei are large, protons repulsion overcomes the strong force and those elements’ nuclei start to decay by emitting energetic particles. The result of these emissions is that they are transformed into more stable elements.



Penetration power of alpha, beta and gamma radiation

Radioactivity means a spontaneous emission of radioactive particles by an unstable nucleus. Atoms which are prone to decay are classified as radioactive. Conversely, an isotope is considered stable if it does not spontaneously transform into another element by radioactive emission.

In the late 19th century Ernest Rutherford was able to identify three common radioactive emissions which were released by radioactive atoms. He was also able to show how they behave in an electric field, which allowed him to find charges of each particle. He named them as alpha, beta and gamma radiation.

Radioactive uranium mineral

Scientist dosimetrist (radiation supervisor) in protective clothing and gas mask with Geiger counter checks the level of radioactive radiation in the danger zone

Nuclear radiation hazard sign

The alpha particles are bare helium nuclei that lost their electrons (He2+). It is represented as α or 2 4α. When an element emits an alpha particle its mass is reduced by 4, and proton number by 2:

$$^{208}_{84}Po \rightarrow {}^{204}_{82}Pb + {}^{4}_{2}\alpha \qquad {}^{233}_{92}U \rightarrow {}^{229}_{90}Pb + {}^{4}_{2}\alpha$$

The above reaction is called a nuclear equation, or nuclear reaction. Highly energetic electrons and positrons are called beta particles or beta rays. Sometimes positrons are termed antielectrons, because they have similar mass like an electron, but they are positively charged. Beta rays are represented as β- for an electron, and β+ for a positron. If they collide with each other, they are annihilated and energy is produced in the form of gamma rays. When an electron is emitted from a nucleus, it transforms a neutron to a proton. Conversely, positron emission results in the transformation of proton to a neutron.

$$^{1}_{0}n \rightarrow {}^{1}_{1}p + \beta^{-}$$
$$^{1}_{1}p \rightarrow {}^{1}_{0}n + \beta^{+}$$

Beta rays could also be represented as -10 e or +10 e. An electron’s (or a positron) mass is negligible compared to the mass of a proton (or a neutron). Therefore we assume that it is 0. Note that, when an atom emits beta rays it does not affect the atomic mass of an element.

$$ {}_{90}^{234}Th \rightarrow {}_{91}^{234}Po + \beta^- $$
$$ {}_{6}^{14}C \rightarrow {}_{7}^{14}N + \beta^- $$
$$ {}_{12}^{23}Mg \rightarrow {}_{11}^{23}Na + \beta^+ $$

Gamma rays are highly energetic photons. Usually, it is released by following alpha or beta emission of an atom. When an atom ejects an alpha or beta particle, a newly formed atom is in the higher energetic state. It has to release a certain amount of energy to be energetically stable. This excess energy is released in the form of gamma rays. In the following example, uranium is transformed into thorium which is in the high-energy state when it is produced. It releases excess energy by gamma rays to be in more stable, low-energy state. Gamma rays do not affect the number of nucleons.

$$ {}_{92}^{234}U \rightarrow {}_{90}^{230}Th + \alpha $$
$$ {}_{90}^{230}Th \rightarrow {}_{90}^{230}Th + \gamma $$

The given graph shows the neutron-to-proton ratios of various isotopes are shown. Isotopes which are located along the black band are stable isotopes. Elements up to lead have at least one isotope which is stable, except two elements technetium Tc and promethium Pm which do not have any stable isotopes. Hydrogen and helium are the only two elements having isotopes with a neutron-to-proton ratio less than 1. Other stable isotopes have neutron-to-proton ratio up to 1.5. However, all elements with an atomic number more than 83 are radioactive.

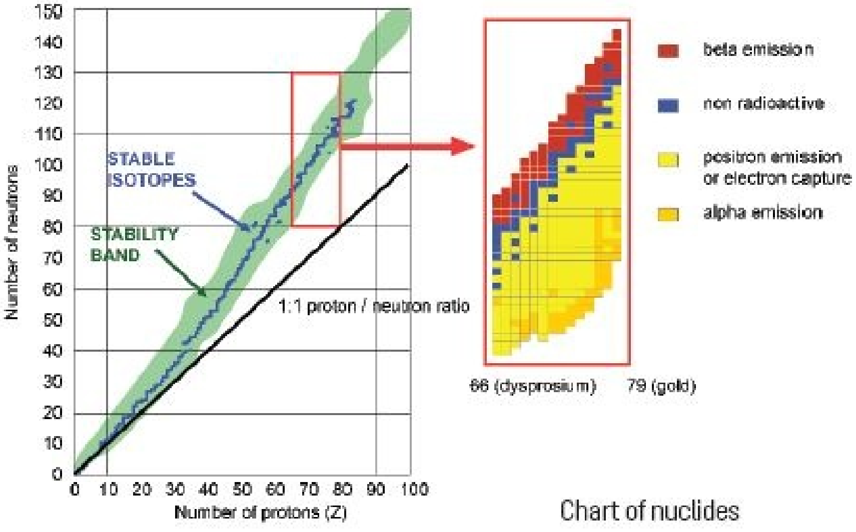


Chart of nuclides

Table 1 *Common emission particles*

Types of decay	Symbol	Chemical symbol	Changes		Example
			Atomic number	Atomic mass number	
Alpha	α	$^{4}_{2}He$	Decreases by 2	Decreases by 4	$^{238}_{92}U \rightarrow ^{234}_{90}U + \alpha$
Beta	$^{-}\beta$	$^{0}_{-1}e$	Increases by 1	No change	$^{234}_{90}Th \rightarrow ^{234}_{91}Pa + ^{0}_{-1}e$
Gamma	γ	$^{0}_{0}\gamma$	No change	No change	$^{234}_{90}Th^{*} \rightarrow ^{234}_{90}Th + ^{0}_{0}\gamma$
Positron	$^{+}\beta$	$^{0}_{+1}e$	Decreases by 1	No change	$^{23}_{12}Mg \rightarrow ^{23}_{11}Na + ^{0}_{+1}e$
Neutron	n	$^{1}_{0}n$	No change	Decreases by 1	$^{87}_{36}Kr \rightarrow ^{86}_{36}Kr + ^{1}_{0}n$

Research time

Open in browser Radiation health effects.

Research about Semipalatinsk Polygon What diseases are caused by radiation?.

Chemistry around us

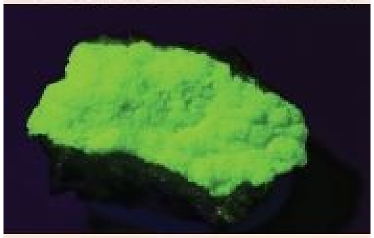
Carbon-14 dating is a method which is used to determine the age of an object by using the radioactive properties of carbon-14. Carbon in nature consists mainly from 12C and 13C isotopes. However, radioactive isotope 14C also exists in trace amounts. It is formed in the upper atmosphere, when cosmic rays interact with nitrogen. Due to the carbon cycle, amount of this radioactive isotope in living organisms is nearly constant, so does in the atmosphere. It starts to decrease exponentially as the organism dies. Knowing the amount of carbon-14 in an ancient organism or an object allows us to determine the age of that organism.

Activity

Marie Curie was a famous chemist and physicist. Do some research on her and write a short text about her life and how she developed her research about radioactivity. Include the following information:

- when/ where she was born/died

- when/how she research about radioactivity
- other achievements in her life



Research time

Open in browser Phet. Alpha decay. A Uranium-238 atom undergoes alpha decay.

What is the other product of the transmutation?

Open in browser Phet. Beta decay. What is the difference between alpha decay and beta decay?

Open in browser Phet. Radioactive Dating Game.

Literacy

1. Find the missing isotope/particle (X and Z) for the following nuclear reactions:

a. $10_{5}B + {}_{0}{}^{1}n \rightarrow X + {}_{2}{}^{4}\alpha$

b. $^{234}{}_{90}Th \rightarrow X + {}_{-1}{}^{0}e$

c. $_{6}{}^{11}C \rightarrow {}_{5}{}^{11}B + Z$

d. $_{14}{}^{27}Si \rightarrow X + {}_{+1}{}^{0}e$

e. $_{6}{}^{17}C \rightarrow X + {}_{-1}{}^{0}e + {}_{0}{}^{1}n$

2. Predict whether the following isotopes of elements likely to emit an alpha, electron or positron.

- ^{30}Na
- ^{20}Na
- ^{120}I

3. Give examples of radioactive substances and describe how radioactivity is used in everyday

4. A radioactive element decays through one positron (+) emission and gives potassium, $_{39}K$. Find the element decayed.

5. A radioactive nucleus $^{5}{}_{2}He$ transmutes into one of its isotopes through a neutron emission. What is the neutron/proton ratio in the new nucleus produced?

6. When an atom of $^{106}{}_{46}Pd$ is bombarded with particles, its nucleus captures one particle and emits one proton and transmuted into Ag. What is the number of neutrons of the Ag atom produced?

Chemistry around us

Positron emission tomography is a technique which uses radioactive isotopes to examine the metabolic processes inside a human body. It works by using a radioisotope inserted to a molecule such as a glucose. Radioisotope is used as a tracer that emits positrons. When these positrons encounter electrons they “cancel” each other by emitting gamma rays, which is what is being observed in PET. After a patient ingests radioactive glucose, it is possible to follow the pathway and destination of that specific molecule. PET is widely used in detecting cancer cells.

Chemistry around us

A synthetic chemical element americium Am (in the form of dioxide) is used in smoke detectors. Alpha particles which are emitted by this element produce an electric current in contact with air molecules, and when smoke molecules disturb this constant electric current, it starts the alarm. This constant amount of alpha radiation in smoke detectors are extremely small in quantity. They do not pose any harm, because they can be stopped by a sheet of paper, or even with the molecules of air. It is not dangerous unless you inhale or ingest it.

Terminology

- operate - әрекет ету / действовать;
- repulsion - серпу / отталкивание;
- emission - шығу / выбросы;
- dosimetrist - дозиметр / дозиметр;
- geiger counter - Гейгер санағышы / счетчик Гейгера;
- prone to - бейім / склонный к;
- decay - ыдырау / распад;
- annihilation - жойылу / уничтожение.

1.3 ELECTRONS LEVELS AND SUBLEVELS. QUANTUM NUMBERS

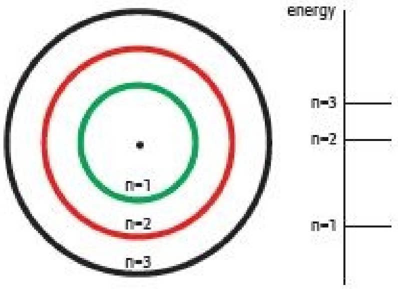
Electrons are negatively charged particles, while protons are positively charged particles. In an atom, why the electrons not collide with protons and stop their rotation around the nucleus? (Re-state)

You will:

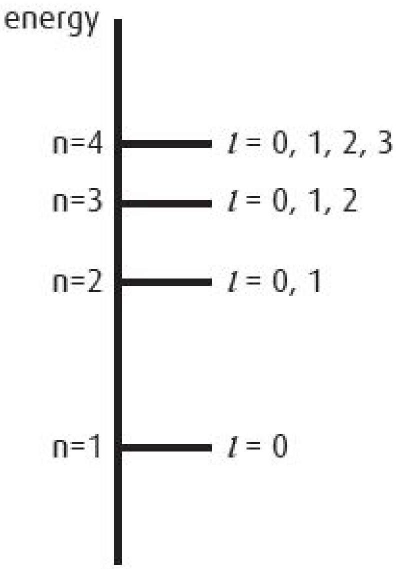
- understand characteristics and significance of quantum numbers;
- distinguish s-, p-, d- and f-orbitals.

Whenever a chemical reaction occurs between atoms, molecules, or ions the species that are being exchanged between atoms are electrons. Nothing happens to the nucleus of an atom. Protons and neutrons remain the same for a particular type of atom during a chemical reaction. How the electrons are responsible for chemical properties of elements? How are they arranged around a nucleus?

Each electron in an atom has its specific location that can be labelled by four quantum numbers, namely, principal quantum number (n), orbital angular momentum quantum number (ℓ), magnetic quantum number ($m\ell$), and spin quantum number (ms).



Electrons are located in shells or energy levels according to their energy



Principal quantum number

Electrons in an atom are located around an atom in shells, or energy levels according to their energies. Principal quantum number determines the energy level and the size of the shell. It is designated by a letter n. It can have values starting from one to infinity. For instance, an electron located in the third shell (or third energy level), n = 3, has higher energy than an electron located in the first shell, n = 1. Moreover, the size of the third shell is bigger than the size of the first shell. Electrons in an atom tend to be in the lowest energetic state, that is to say, they are located in the shells which are closest to the nucleus. In addition, the number of electrons which a particular shell can occupy increases as the n value increases.

In one-electron hydrogen atom, the only electron is located in the first shell. However, it can be displaced into the second shell by increasing its energy (if we give enough energy by electromagnetic radiation). As we put more energy, it will locate itself to a higher values of n. If the energy is high enough for n value to reach infinity, then an electron is ejected from an atom. Conversely, an electron located in the upper shell can be displaced to a lower shell (provided that the lower shell is vacant), by emitting energy in the form of photons.

Secondary quantum number

Location of electrons in a specific shell can be further described by subshells. As the value of n increases, the number of available subshells also increases. Subshells are described by orbital angular momentum quantum number, ℓ. Subshells with different values have different shapes of orbitals. You can think of an orbitals as a room where electrons are located. Orbital angular momentum quantum number can have values of ℓ = 0, 1, 2, 3 .... n-1 for specific value of n. For instance, a second shell (n=2) can have two subshells with value of ℓ =0 and ℓ=1, which means it contains two differently shaped orbitals. ℓ values can also be labelled by letters s, p, d and f (0,1,2 and 3 respectively). The shapes of orbital angular momentum quantum numbers are shown in the picture. The nucleus in these models are located on the origin of Cartesian coordinate plane.

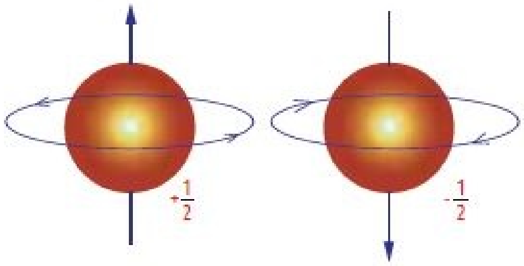
Magnetic quantum number

Magnetic quantum number, which is designated by $m\ell$ is what determines the orientation and the number of orbitals. Atomic orbitals having the same value of orbital angular momentum quantum number can be oriented differently. As you can see from picture, s-orbitals (ℓ = 0) are spherical, which means they can have only one value of $m\ell$. While p electrons (ℓ = 2 value), can have 3 orbitals with different $m\ell$ values (px, py, pz). In general, $m\ell$ takes values of $m\ell = -\ell, -\ell+1,...0..., +\ell-1, +\ell$ for specific ℓ value. For instance, if ℓ = 3, then $m\ell$ = -3, -2, -1, 0, +1, +2, +3.

Each orbital can have maximum of 2 electrons. Hence, s-orbitals with ℓ = 0, contain only one orbital with $m\ell$ = 0 that can have only 2 electrons. However, p-orbitals with ℓ = 1, contain three orbitals with m = -1, 0, +1 that can accomodate 6 electrons.

Spin quantum number

The fourth quantum number spin quantum number, ms, determines the spin of electrons. You can think of it as electron’s spin on its own axis. It can have values of either +1/2 (counterclockwise, ↑) and -1/2 (clockwise, ↓). Each orbital with their electrons can be represented by boxes.



Magnetic spin quantum number

n	1		2								3																	
ℓ	0		0		1						0		1						2									
mℓ	0		0		-1		0		+1		0		-1		0		+1		-2		-1		0		+1		+2	
ms	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

Literacy

1. Write down the values of n, l and ml for the 5s and 3d subshells?

2. How many electrons can have the same set of given quantum numbers:

a. $n = 2, l = 1$

b. $n = 3$

c. $n = 4, l = 3, ml = -1$

3. Write the electron configuration for the elements Mg, Ar, P and Sc.

4. Which of these following set of quantum numbers are impossible for an electron?

a. $n=3, l=3, ml=0, ms=+\frac{1}{2}$

b. $n=2, l=0, ml = -1, ms = -\frac{1}{2}$

c. $n=3, l=2, ml = +1, ms = -\frac{1}{2}$

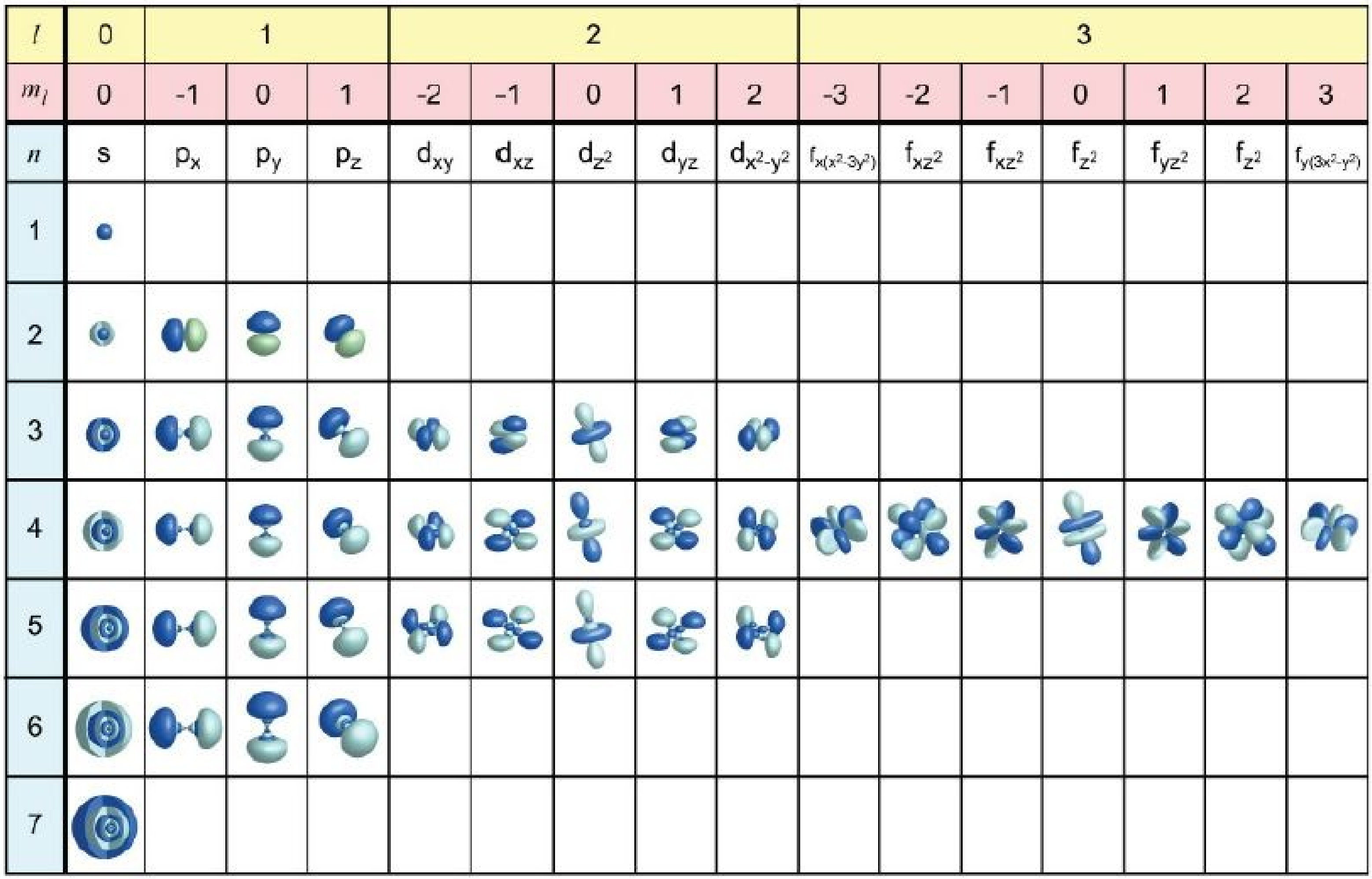
Research time

Open in browser Phet. Quantum Wave Interference.

What does it mean that the electron has a dual nature (particle and wave properties)?

Terminology

- quantum - квант
- photon - фотон
- spin number - спин саны / число спинов



Shapes of orbitals

1.4 ELECTRON CONFIGURATION

Why is the Periodic Table arranged by atomic number and not atomic mass?

You will:

- apply the principle of minimum energy (the Pauli principle), the rule of Hund rules for filling electronic orbitals;
- write electron configuration of elements of the periodic table.

We know that electrons are located in the form of clouds around a nucleus. In previous chapter we covered the concept of energy levels, orbitals or subshells, the orientation of orbitals and spin of the electrons. In this chapter we will learn how these electrons are arranged around the nucleus.

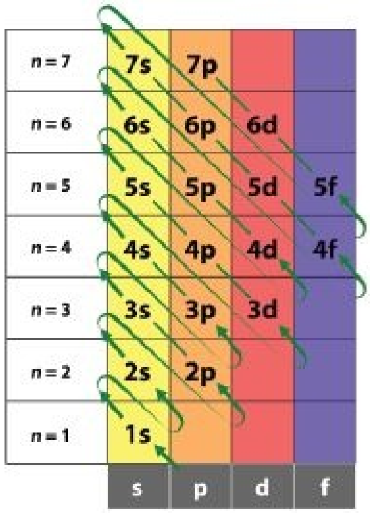
The electron of a hydrogen atom in its ground state is located in the nearest orbital to the nucleus. But, what about the electron distribution of the atoms with more than one electron? Answering this question in 1925, Wolfgang Pauli stated his exclusion principle: 'In the same atom, two electrons may not have identical sets of all quantum numbers.'

According to this principle, the quantum numbers, n, ℓ, mℓ, and ms, can never be identical for two electrons in an atom. This means that at least one of the quantum numbers must be different. For example, even if two electrons have identical values for n, ℓ and mℓ (as a result of being in the same orbital), their magnetic spin quantum numbers must be different. That is, these electrons are said to have opposing spins. In fact, we have already mentioned that each electron may be described by a set of four quantum numbers;

- n shows the shell and the relative average distance of the electron from the nucleus
- l shows the subshell and the shape of the orbital for the electron
- mℓ represents the orientation of the orbital in spaces
- ms refers to the spin of the electron.

The Aufbau Principle

The Aufbau principle basically states that the lowest energy orbitals are filled first. 1s orbital has the lowest energy, so it is first to be filled, followed, in order, by 2s, 2p, 3s... This ordering was first stated by Wolfgang Pauli and is called the Aufbau principle ('aufbau' means 'building up' in German)



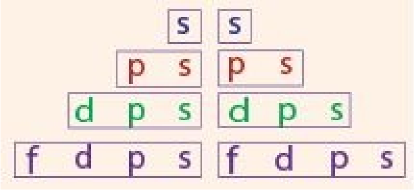
Order orbitals in writing electron configuration

The Hund's Rule

Different orbitals with identical energy (those in the same subshell) are known as equal energetic orbitals. For example the orbitals of p subshell px, py and pz are of identical energy. Since all electrons carry the same electrical charge, they tend to be as far as possible from each other. Thus, Hund's rule states that the electrons are distributed among the orbitals of a subshell of the same energy in a way that gives the maximum number of unpaired electrons with parallel spin. The term 'parallel spin' means that all the unpaired electrons spin in the same direction, and all of the ms values of these electrons have the same sign. In some cases, at higher quantum levels, since the energies of some subshells are very close to each other, there may not be any coherence between the order of filling the orbitals and the order of increasing the energies of the orbitals. For example, the 4s orbital has a lower energy than that of a 3d orbital. That is, the 4s orbital is filled before the 3d orbital. The order of filling of orbitals is derived as a result of experiments in spectroscopy and magnetism. The order of filling electrons in atomic orbitals, with a few exceptions, is roughly as follows.

1s2, 2s2, 2p6, 3s2, 3p6, 4s2, 3d10, 4p6, 5s2, 4d10, 5p6, 6s2, 4f14, 5d10, 6p6, 7s2, 5f14, 6d10, 7p6

In order to remember and derive this order easily, the method illustrated by the table is very useful. When following the arrows from top to bottom, the order given above is obtained.



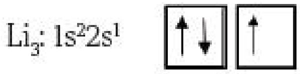
Electron configuration of elements

Hydrogen atom contains only 1 electron that occupies the shell with the lowest energy level n=1. A shell with n=1 can have a value of $\ell=0$ (s-orbital), which can simply be represented as 1s. A box is used to represent orbitals(magnetic quantum number mℓ), and each orbital can allocate maximum of two electrons. The only electron of hydrogen would be allocated to this 1s orbital within a block with spin up, and represented as 1s1.

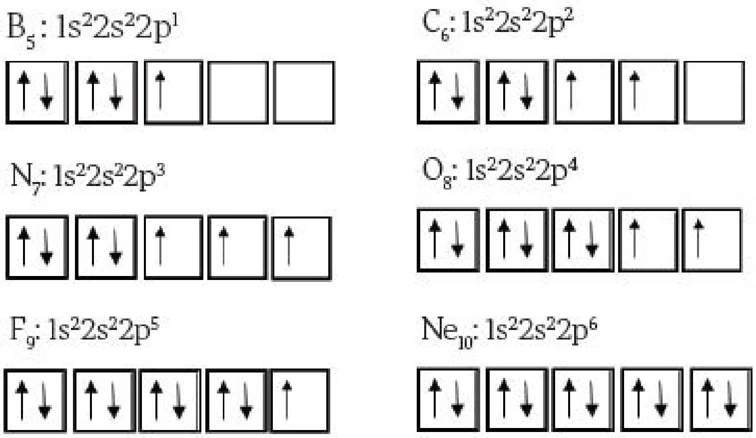
Helium atom, which contains 2 electrons will also be allocated to 1s orbital as it has the lowest energy.

When an orbital contains two electrons, they should be paired to be energetically stable (with different ms values). The rule we have just followed is Aufbau principle.

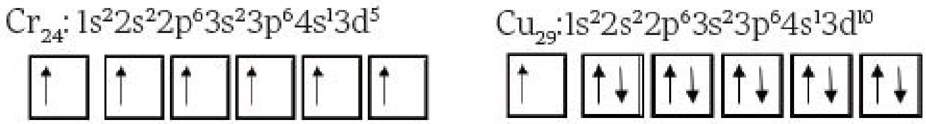
In the 2nd row elements, 1st shell is filled in the same order as in the helium. We know for sure that other electrons have to start to occupy the second shell with n=2. The subshell with 2s (n=2, ℓ=0) is filled up next rather than 2p (n=2, ℓ=1) because 2s is lower in energy than 2p.



There are three orbitals within a subshell 2p (mℓ = -1, 0, +1), so they are represented together, because they are equal in energy. These types of orbitals with equal energy are called degenerate orbitals.



Electron configuration following neon obeys the Aufbau principle. However, there are some exceptions to the Aufbau principle. For instance, experimental observations show that in chromium and copper one electron located in 4s2 is displaced to 3d orbitals to give more energetically stable electronic state.



You may have noticed that no two electrons arranged in an atom can have the same set of four quantum numbers. For example, in helium atom, two electrons may have 3 set of the same n = 1, ℓ = 0, and mℓ = 0 values. However these two electrons have different ms values of +½ and -½.

Activity

Wolfgang Pauli investigated the quantum mechanics.

Write the short text about the quantum mechanics. Include the following information:

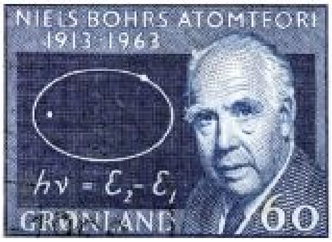
- when/how he research about quantum numbers

- where/when he works

Research time

Open in browser Bohr–Einstein debates.

Research ideas of Niels Bohr and Albert Einstein. What is the difference between Niels Bohr's and Albert Einstein's theories of quantum mechanics?



Literacy

1. Write down the electron configurations of the following elements:

Ca, Co, Zn, Br, Ar

2. Find the elements that has the following valence shell electron configuration:

- ...$2s^2 2p^2$;
- ...$3d^5 4s^2$;
- ...$3d^{10} 4s^1$;
- ...$3s^2 3p^6$

3. Write down the electron configuration of the elements which

have the following characteristics:

a) An element which has total number of electrons with orbital angular momentum quantum number, l=1 is 9;

b) An element which has total number of electrons with principal quantum number n=2 is 10;

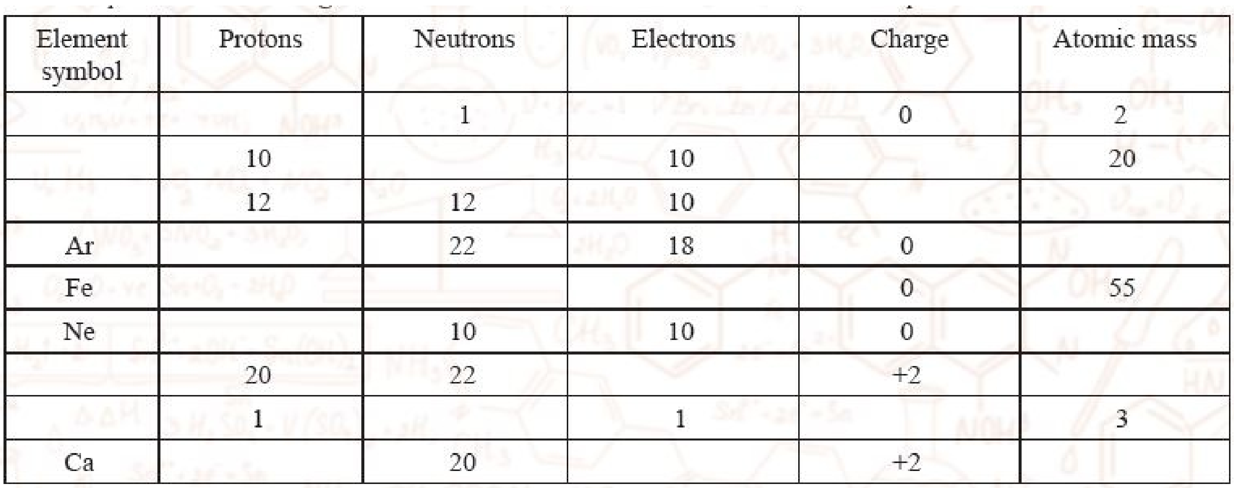
c) An ion $_{20}X^{2+}$;

Terminology

- configuration – конфигурация/ конфигурация;
- direction – бағыт / направление;

QUESTIONS AND PROBLEMS

1. Complete the following table and find which of these elements are isotopes:



Element symbol	Protons	Neutrons	Electrons	Charge	Atomic mass
		1		0	2
	10		10		20
	12	12	10		
Ar		22	18	0	
Fe				0	55
Ne		10	10	0	
	20	22		+2	
	1		1		3
Ca		20		+2	

2. Natural isotopes and their natural abundances are given. Find the average relative mass for the following elements:

a. 10B 19.9%, 11B 80.1%

b. 24Mg 78.99%, 25Mg 10.00%, 26Mg 11.01%

c. 93Nb 100%

d. 79Br 50.69%, 81Br 49.31%

3. The relative atomic mass of silver is 107.87. Find the abundances for the isotopes of silver, 107Ag and 109Ag.

4. Calculate the number of protons for the following compounds:

a. NH3 b. BaCl2 c. C6H12O6 d. CH4

5. Which of the following quantum numbers are not possible for a specific electron in an atom?

a. n = 7, l = 1, ml = -2, ms = +1/2

b. n = 3, l = 2, ml = +2, ms = +1/2

c. n = 3, l = 2, ml = -2, ms = -1/2

d. n = 5, l = 0, ml = -1, ms = -1/2

e. n = 3, l = 0, ml = 0, ms = 0

6. How many electrons can be found in each of the following set of quantum numbers?

a. n = 3, l = 0

b. n = 3, l = 1

c. n = 3, l = 2, ml = +2

d. n = 4, l = 0, ml = 0, ms = -1/2

e. n = 2

7. Place the following atomic orbitals in increasing of their energy:

a. 1s, 2s, 4s, 3s

b. 4s, 4p, 4d, 4f

c. 1s, 2p, 3d, 4f

d. 2s, 3d, 3s, 4d

e. 1s, 3p, 4p, 4f

8. Represent the following primary and secondary quantum numbers as 1s, 2p, 3d, etc.

a. $n = 2, l = 1$

b. $n = 5, l = 4$

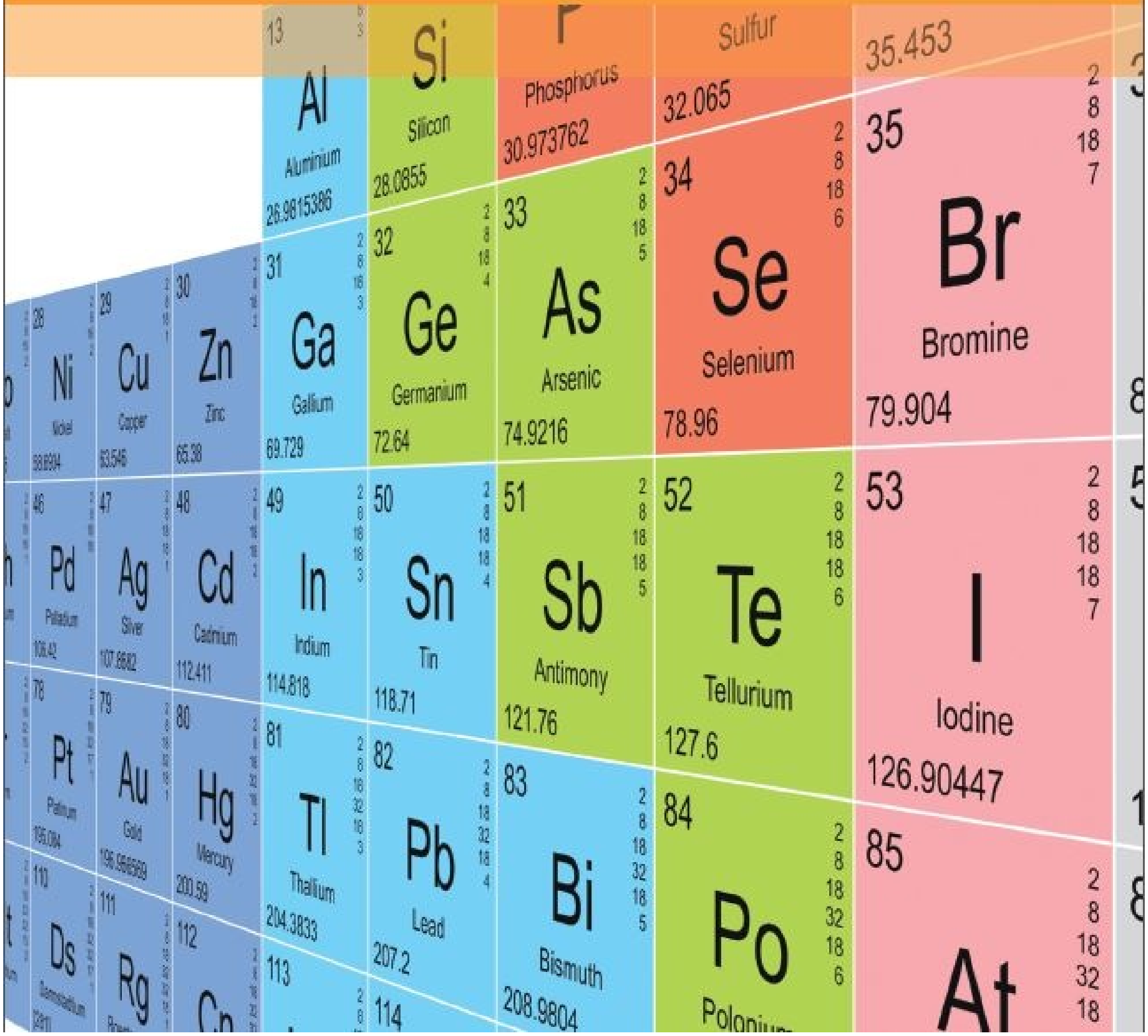
c. $n = 3, l = 1$

d. $n = 4, l = 3$

e. $n = 1, l = 0$

2 CHAPTER

PERIODICITY



CHAPTER 2: PERIODICITY

2.1 THE PATTERN OF CHANGING THE PROPERTIES OF ELEMENTS IN PERIODS AND GROUPS

D.I.Mendeleyev in 1869 predicted the discovery of some unknown elements. How is it possible nowadays to discover a new element?

You will:

- describe the patterns of change in the properties of atoms of chemical elements;
- know the terms: atomic radius, ionization energy, electron affinity, electronegativity and degree of oxidation.

The pattern of changing of the properties (or periodic trend) of elements is a predictable change in a particular direction. Understanding a trend among the elements enables you to make predictions about their chemical behavior. These trends in properties of the elements in a group or a period can be regarding electron configurations. Let’s examine some trends in the properties of elements in the Periodic table.

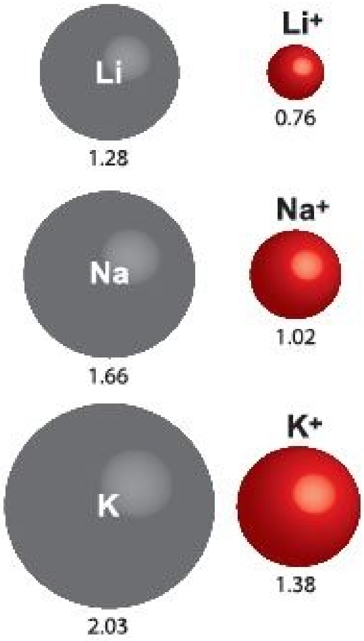
Atomic radius

The physical properties of the elements, such as melting point, boiling point and density are related to the atomic radius of the elements. Also, atomic radius directly affects the ability of an atom to gain and lose electrons. The atomic radius is practically defined by assuming the shape of the atom as a sphere. The atomic radius is the distance between the nucleus and the outermost electron.

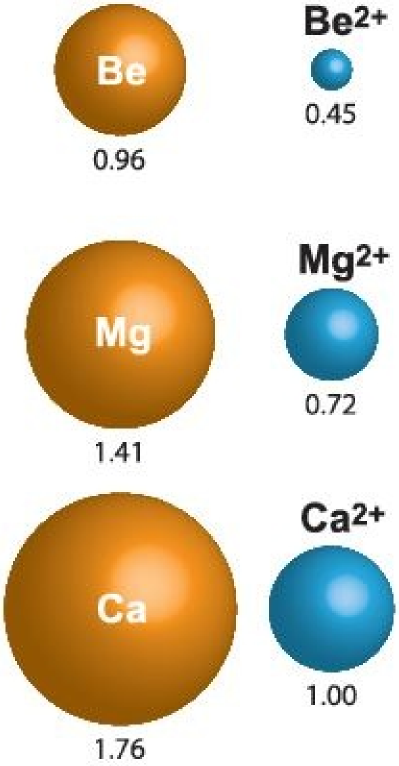
Atomic Radius within a Group

Since the number of shells increases in the same group from top to bottom (by the period number increases), the atomic radius also increases. This means that the electron cloud around the nucleus becomes larger. The increase in the number of electrons causes them occupy a new energy level and orbitals.

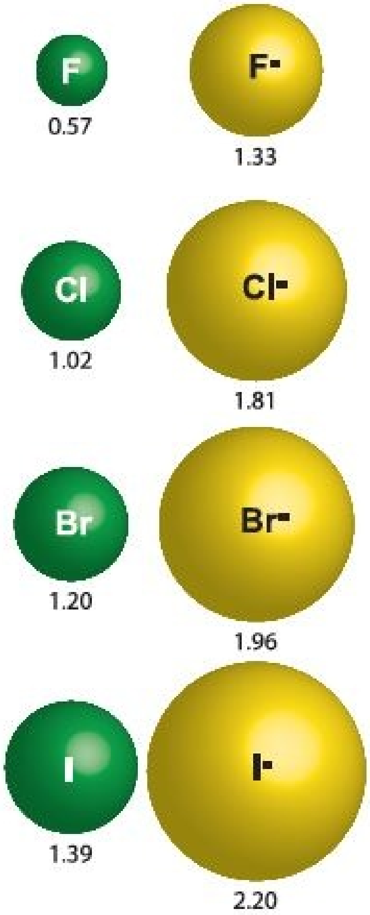
A higher energy level is always further from the nucleus. Within a period, if the number of protons and electrons increases, the nuclear attraction force increases. This attraction force prevents an enormous increase in atomic radius.



Atomic radii of alkali metals and their ions (values in 10^{-10} m)



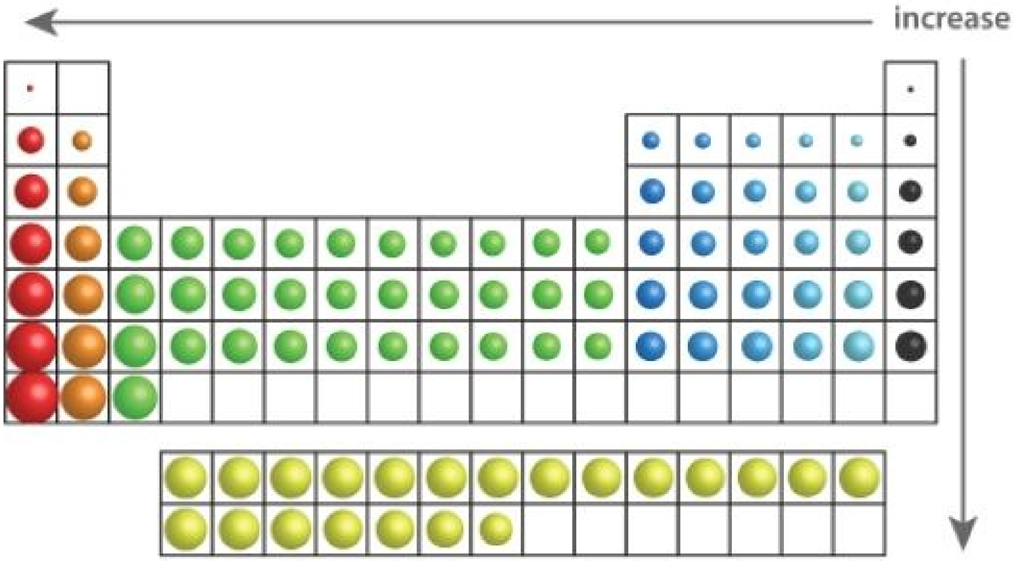
Atomic radii of alkaline earth metals and their ions (values in 10^{-10} m)



Atomic radii of halogens and their ions (values in 10^{-10} m)

Atomic Radius Within a Period

The atomic radius usually decreases from left to right in a period. It may be thought that the atomic radius has to increase because of the increase in the number of electrons in a period (in the same shell). However, the number of protons also increases by as much as that of electrons. Increasing the number of protons increases the nuclear attraction force on the electrons. Thus, since the intensity of nuclear attraction force per one electron increases, the atomic radius decreases from left to right in a period.



Atomic radius increases from right to left and from top to the bottom.

Ionization energy

Ionization energy is the energy required to remove an electron from an atom in its ground state in the gas phase. This energy shows the degree of attractive force that the nucleus has on the electron. In order to accomplish ionization, the atom can be in neither a solid state nor a liquid state. The removable electron is the most loosely held electron.

The amount of energy required to remove one electron from the valence shell of a neutral atom in a gaseous state is defined as the first ionization energy and denoted by I1. The values of the first ionization energy, I1, and corresponding ionization equations for the elements are given below.

$Na_{(g)} + 495\ kJ \rightarrow Na^{+}_{(g)} + e^{-}$ $I_1 = 495.8\ kJ/mol$

$Mg_{(g)} + 737.7\ kJ \rightarrow Mg^{+}_{(g)} + e^{-}$ $I_1 = 737.7\ kJ/mol$

$F_{(g)} + 1681.0\ kJ \rightarrow F^{+}_{(g)} + e^{-}$ $I_1 = 1681.0\ kJ/mol$

$Ne_{(g)} + 2080.6\ kJ \rightarrow Ne^{+}_{(g)} + e^{-}$ $I_1 = 2080.6\ kJ/mol$

The energy required to remove the second electron and the third electron are called the second ionization energy (I2) and the third ionization energy (I3), respectively.

$X_{(g)} + \text{Energy} \rightarrow X^{+}_{(g)} + e^{-}$ (1st ionization energy)
$X^{+}_{(g)} + \text{Energy} \rightarrow X^{2+}_{(g)} + e^{-}$ (2nd ionization energy)
$X^{+2}_{(g)} + \text{Energy} \rightarrow X^{3+}_{(g)} + e^{-}$ (3rd ionization energy)

Ionization Energy within a Group

As the atomic radius increases from top to bottom in a group, the valence electrons become further away from the nucleus and the nuclear attraction forces on these electrons decrease. Therefore, as the atomic radius increases, the amount of energy required to remove an electron decreases. As a result, we can say that within a group ionization energy of elements decrease from top to bottom.

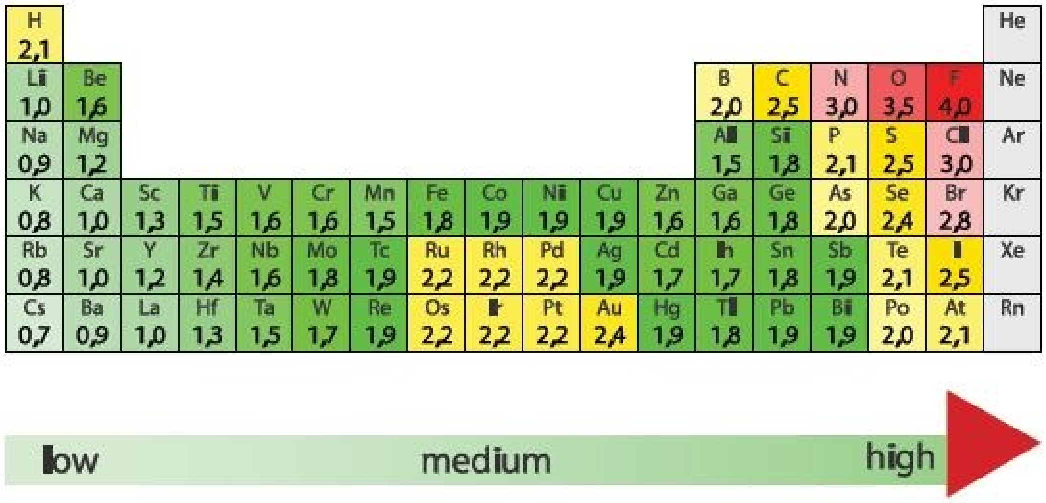
Ionization Energy within a Period

In a period, since the atomic radius decreases from left to right, the ionization energy increases. The elements of group 1 (alkali metals), include elements which have the greatest atomic radii; therefore, the ionization energies of alkali metals are the lowest in every period. The elements of noble gases (group 18) have the highest ionization energies, which means that the noble gases have a very stable electronic structure.

Electronegativity

Electronegativity is a measure of an atom’s ability to attract electrons from a covalent bond in its molecule. The electronegativity of an atom depends on the charge of the nucleus and the distance between the nuclei and the electrons of a covalent bond. Therefore, electronegativity is closely related to ionization energy which expresses the ability of an atom to attract or lose electrons respectively.

Electronegativity is a relative quantity and it does not have a unit. Today, the most commonly used electronegativity scale today is Linus Pauling's scale, which is based on the values of bond energies. According to this scale, the most active metal, francium, has a 0.7 value and the most active nonmetal fluorine has a 4.0 value. The electronegativity value of the other elements is between 0.7 and 4.0.



H 2,1																	He
Li 1,0	Be 1,6											B 2,0	C 2,5	N 3,0	O 3,5	F 4,0	Ne
Na 0,9	Mg 1,2											Al 1,5	Si 1,8	P 2,1	S 2,5	Cl 3,0	Ar
K 0,8	Ca 1,0	Sc 1,3	Ti 1,5	V 1,6	Cr 1,6	Mn 1,5	Fe 1,8	Co 1,9	Ni 1,9	Cu 1,9	Zn 1,6	Ga 1,6	Ge 1,8	As 2,0	Se 2,4	Br 2,8	Kr
Rb 0,8	Sr 1,0	Y 1,2	Zr 1,4	Nb 1,6	Mo 1,8	Tc 1,9	Ru 2,2	Rh 2,2	Pd 2,2	Ag 1,9	Cd 1,7	In 1,7	Sn 1,8	Sb 1,9	Te 2,1	I 2,5	Xe
Cs 0,7	Ba 0,9	La 1,0	Hf 1,3	Ta 1,5	W 1,7	Re 1,9	Os 2,2	Ir 2,2	Pt 2,2	Au 2,4	Hg 1,9	Tl 1,8	Pb 1,9	Bi 1,9	Po 2,0	At 2,1	Rn

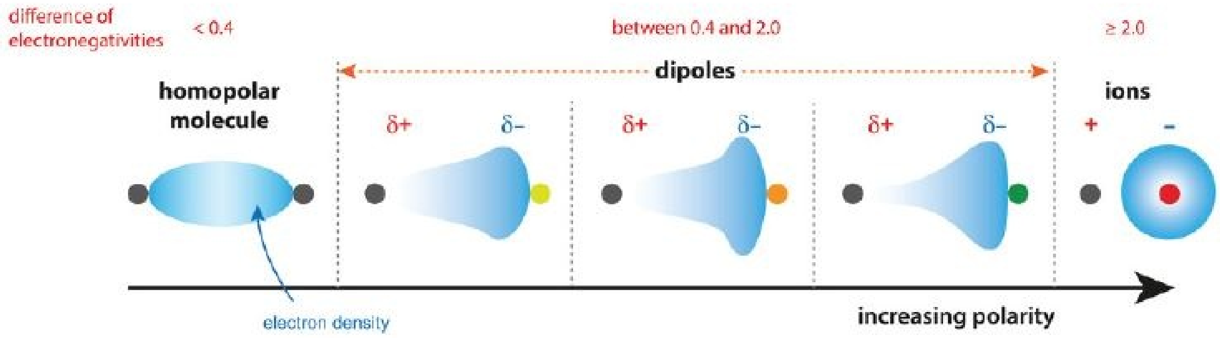
Periodic table of elements with electronegativity values

The electronegativity of an atom depends on the radius of the atom. The atomic radius decreases and attraction exerted on valence electrons by the nucleus increases from left to right in a period. Atomic radius increases and attraction exerted on valence electrons by nucleus decreases from top to bottom. Therefore, electronegativity increases from left to right and decreases from top to bottom in the periodic table.

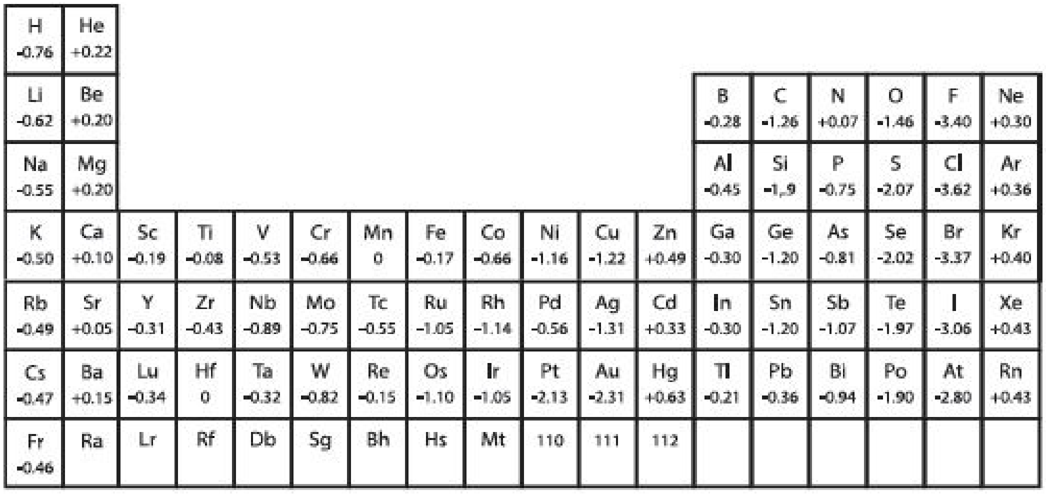
Electron affinity

The energy of the affinity of an atom for an electron, or simply electron affinity (ε), is the energy released or absorbed during the addition of an electron to a free atom in its ground state, transforming it into a negative ion A- (the affinity of an atom for an electron is numerically equal, but opposite in sign of the ionization energy of the corresponding isolated singly charged anion).

Electron affinity changes regularly by with the nature of the electronic structures of the atoms of the elements. It increases from left to right in a period and from bottom to top in a group.



Polarity of dipoles depends on electronegativity



H -0.76	He +0.22																
Li -0.62	Be +0.20											B -0.28	C -1.26	N +0.07	O -1.46	F -3.40	Ne +0.30
Na -0.55	Mg +0.20											Al -0.45	Si -1,9	P -0.75	S -2.07	Cl -3.62	Ar +0.36
K -0.50	Ca +0.10	Sc -0.19	Ti -0.08	V -0.53	Cr -0.66	Mn 0	Fe -0.17	Co -0.66	Ni -1.16	Cu -1.22	Zn +0.49	Ga -0.30	Ge -1.20	As -0.81	Se -2.02	Br -3.37	Kr +0.40
Rb -0.49	Sr +0.05	Y -0.31	Zr -0.43	Nb -0.89	Mo -0.75	Tc -0.55	Ru -1.05	Rh -1.14	Pd -0.56	Ag -1.31	Cd +0.33	In -0.30	Sn -1.20	Sb -1.07	Te -1.97	I -3.06	Xe +0.43
Cs -0.47	Ba +0.15	Lu -0.34	Hf 0	Ta -0.32	W -0.82	Re -0.15	Os -1.10	Ir -1.05	Pt -2.13	Au -2.31	Hg +0.63	Tl -0.21	Pb -0.36	Bi -0.94	Po -1.90	At -2.80	Rn +0.43
Fr -0.46	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	110	111	112						

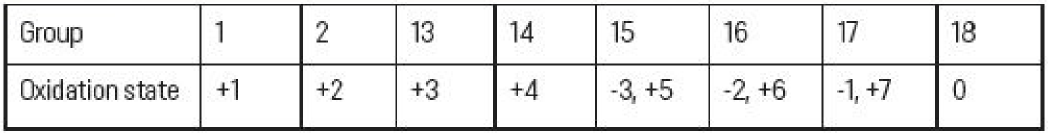
Electron affinity of elements

Oxidation state number

Oxidation state (or charge) is a conditional charge of the atoms of a chemical element in a compound, calculated from the assumption that all bonds have an ionic type.

A charge can have a positive, negative or zero value, so the algebraic sum of the degrees of oxidation of elements in a molecule with the number of their atoms is 0, and in the ion - the charge of the ion. Main group elements have same oxidation state within a group. Example. 1st group alkali metals have common oxidation state +1. Charge increases from left to right in periods of main group elements.

Table 2 *Some common oxidation states of groups 1, 2 and 13-18*



Group	1	2	13	14	15	16	17	18
Oxidation state	+1	+2	+3	+4	-3, +5	-2, +6	-1, +7	0

Research time

Open in browser ptable (Dynamic periodic table).

Choose the tab "Properties (Ionization, Radius)". Compare the ionization energies and radii of chemical elements.

- Which of the atomic radii has the highest and lowest atomic radii of an element?

- How does atomic size affect reactivity?

Research time

Open in browser Fluorine and its chemical properties. Research chemical properties of F2 gas with acids.

- What is the reason why fluorine is the best oxidizing agent?

- Why is the electronegativity of fluorine higher than oxygen?

Chemfact

Most isotopes of superheavy elements are unstable and undergo decays in a very short time. Thus, the recently discovered moscovium Mc has a half-life of only about 220 milliseconds.

Literacy

1. Does electronegativity have any relationship to ionization energy? Explain.

2. How does electronegativity change in a group and period of the periodic table?

3. Write down the elements 12Mg, 14Si, 17Cl, and 9F in order of decreasing electronegativity.

4. Compare the elements 4Be, 5B, 7N and 8O in terms of their first ionization energies.

Terminology

- pattern - сипаты / характер;
- enable - қосу / включить;
- ability - қабілеттілік / способность;
- ionization - иондану / ионизация;
- accomplish - орындау / выполнить;
- further - бұдан кейін / в дальнейшем;
- affinity - сәйкестік / сродство.

2.2 ACIDITY AND BASICITY PROPERTIES OF INORGANIC COMPOUNDS

The similarity between B and Si is the explosive combus tion of their hydrides (B_2H_6 and Si_4H_{10}) in air. Explain why hydrides of B and Si are unstable.

You will:

- explain the patterns of changes in the acidic and basic properties of oxides, hydroxides and hydrogen compounds of chemical elements by periods and groups.

Amphoteric compounds

Some metals form amphoteric oxides or hydroxides. Amphoteric compounds of such elements can react with both acids and bases. The product is salt and water. Examples of amphoteric metals: Be, Al, Zn, Ga, Sb, Sn, and Pb. These metals form amphoteric oxides and hydroxides.

Amphoterism directly depends on the oxidation state of an element. Some elements may have a variety of oxidation numbers. Therefore, one oxide may exhibit only basic properties while another one exhibits acidic properties. For instance, chromium has three different oxides: CrO is basic, Cr2O3 is amphoteric and CrO3 is acidic.

Cobalt (II) oxide

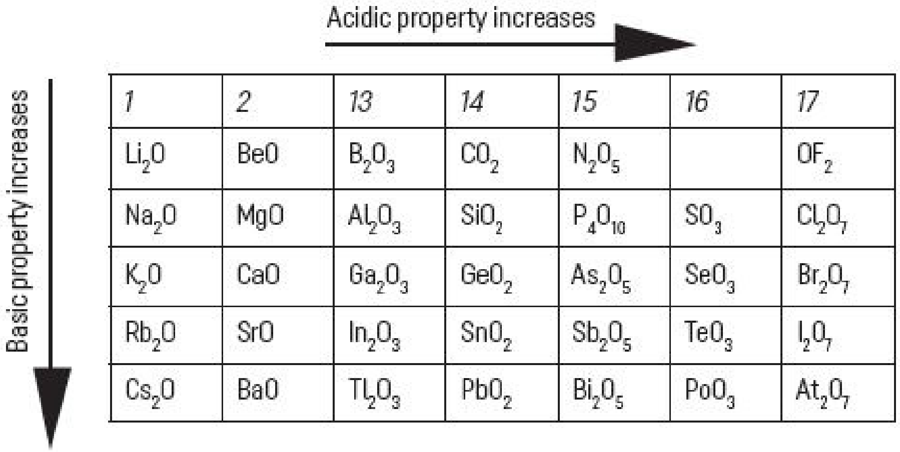
Chromium (III) oxide

Acidity and basicity of oxides

The acidity and basicity of an oxide of an element depend on the electronegativity of that element. The greater the electronegativity, the more acidic the oxide of the element, and the less the electronegativity, the more basic the oxide of the element. Let us examine the oxides of the main group elements of the third period. These oxides, from group 1 to 17, are Na2O, MgO, Al2O3, SiO2,

P2O3, SO2 and Cl2O7. Na2O and MgO are basic oxides, ZnO and Al2O3 are amphoteric oxides and SiO2, P2O3, SO2 and Cl2O7 are acidic oxides. Thus, the acidity of the elements increases and the basicity of the elements decreases from 1st through 17th in the third period. In general, the acidity of oxides of the elements increases from left to right in a period, and the basicity of the oxides of the elements decreases.

Since the electronegativity of elements decreases from top to bottom in a group, the basicity of the oxides of the elements increases and the acidity of the oxides of the elements decreases.



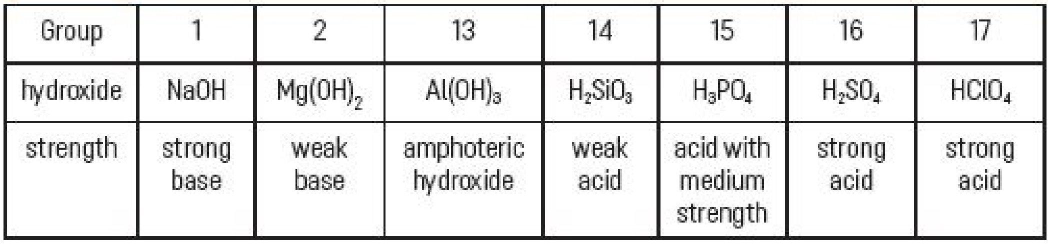
1	2	13	14	15	16	17
Li_2O	BeO	B_2O_3	CO_2	N_2O_5		OF_2
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

Acidic and basic properties of oxides

Acidity and basicity of hydroxides

The changes in acidic and basic properties of hydroxides are similar to their oxides. In a period with an increase in the atomic number (from left to right), the basic properties of the hydroxides gradually decrease, and the acidic properties increases.

Table 3 *Acidic and basic properties of compounds*



Group	1	2	13	14	15	16	17
hydroxide	$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	H_2SiO_3	H_3PO_4	H_2SO_4	$HClO_4$
strength	strong base	weak base	amphoteric hydroxide	weak acid	acid with medium strength	strong acid	strong acid

In a group with an increase of atomic number (from top to bottom), the basic properties of the hydroxides of the elements increases and acidic decreases.

$$HClO3 > HBrO3 > HIO3$$

Acidity and basicity of hydrogen compounds

In groups from the top down (HF - HCl - HBr - HI), negatively charged anions attractions of hydrogen with smaller force - the process of splitting off hydrogen ions becomes easier and the acidic properties of hydrogen compounds increase.

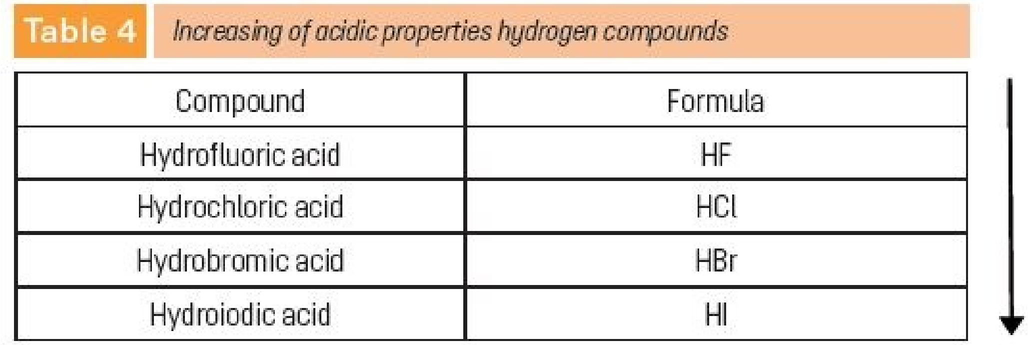


Table 4 *Increasing of acidic properties hydrogen compounds*

Compound	Formula
Hydrofluoric acid	HF
Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI

Chemistry around us

Boric acid, H3BO3 [or B(OH)3] is used as external disinfec tant, eyewash, and insecticide.

Chemistry around us

Hydrogen peroxide, H2O2 is used as an oxidizing agent, disinfectant, and bleach, and in the production of peroxy compounds for polymerization.

Literacy

1. Which member of each pair gives the more basic solution in water:

- BaO or SO_3;
- MgO or BaO;
- CO_2 or SO_2;
- P_2O_5 or Li_2O?

2. Which member of each pair gives the more acidic solution in water:

- CO_2 or SrO;
- SnO or SnO_2;
- Cl_2O_7 or Na_2O;
- SO_2 or MgO?

3. Complete and balance the following equations:

- An active metal reacting with acid,

$Ca(s) + HCl(aq) \rightarrow$

- An alkali metal hydride reacting with water,

$KH(s) + H_2O(l) \rightarrow$

4. Which member of the following gives the more acidic solution in water?

- CO_2
- SiO_2
- GeO_2
- SnO_2

5. Which member of the following gives the more basic solution in water?

- CaO
- K_2O
- Co_2O_3
- ZnO
- As_2O_3

Research time

Write the chemical reactions of amphoteric oxides with acids and bases.

- What is the acidic strength order of the oxo-acids of chlorine: $HClO_2$, $HClO$, $HClO_4$?

- Write the chemical formulas of hydrogen compounds of elements by period.

- Compare the properties of water to those other group 16 hydrides?

Terminology

- amphoteric - екідайлы / амфотерный;
- splitting - ажырау, ыдырау / расщепление;
- variety - әртүрлілік / разнообразие.

2.3 TRENDS IN THE REDOX PROPERTIES OF COMPOUNDS IN PERIODS AND GROUPS

Why are redox reactions important?

You will:

- predict the patterns of changes in the properties of compounds of chemical elements by period and group;
- predict the properties of chemical elements and their compounds by position in the periodic system.

Periodicity of oxidation-reduction properties

The oxidation-reduction properties of the elements also exhibit periodic changes. The periodicity of these changes is as follows: the elements occupying the left part of the periodic table, that is, the alkali and alkaline-earth metals are strong reducing agents. Then, as you move to the right along each period, reducing properties decreases and oxidizing properties increases.

Finally, group 17 are strong oxidizers. Let us now consider this pattern in somewhat more detail. The reducing properties of the metals are characterized by low ionization energy, low electron affinity and low electronegativity.

Examples of reducing properties of metals:

1. React with oxygen

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

2. React with halogens

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Reactions which are given above are examples of reducing properties of metals since in each case metals easily loses electrons:

$$Mg \rightarrow Mg^{2+} + 2e^-$$
$$Na \rightarrow Na^{1+} + e^-$$

Oxidizing properties of elements of the 17th group, which are placed on the right side of the table, are characterized by high ionization energy, high electron affinity and high electronegativity.

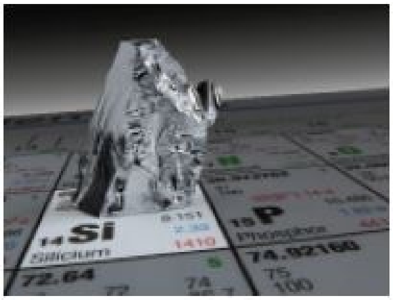
For instance, chlorine element has properties of a strong oxidizer. It reacts violently with hydrogen in the sunlight, forming hydrogen chloride.

p-elements, which are closer to the middle part of the periods, show weak reducing and (or) weak oxidizing properties. For example, the silicon belonging to 14th group reacts slowly with oxygen, forming an oxide.

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$

The nitrogen belonging to the 15th group can act both as a weak reducer and as a weak oxidizer. For example, it behaves as a weak reducing agent in reaction with oxygen:

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$



Pure silicon

Liquid nitrogen

In contrast, in a reaction with hydrogen, nitrogen behaves as a weak oxidizer:

$$\mathrm{N2(g) + 3H2(g) \rightarrow 2NH3(g)}$$

The transition elements have the properties of weak reducing agents. For example, hot iron reacts with water vapor to form hydrogen:

$$\mathrm{Fe(s) + H2O(g) \rightarrow FeO(s) + H2(g)}$$

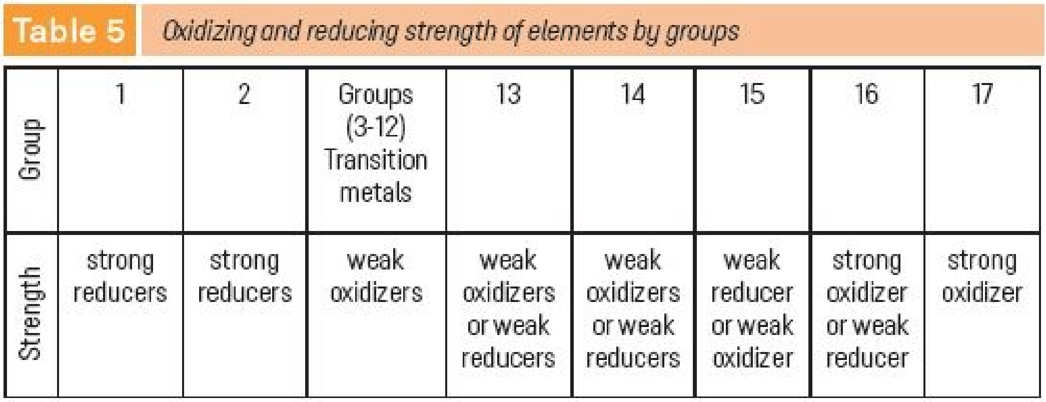
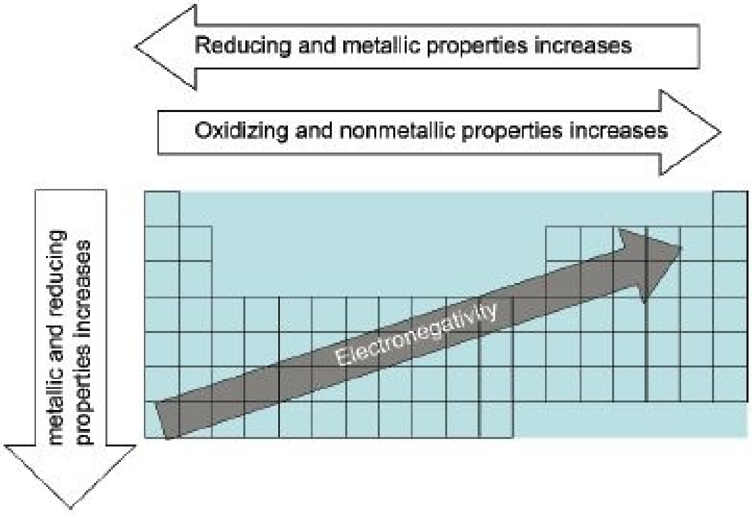


Table 5 *Oxidizing and reducing strength of elements by groups*

Group	1	2	Groups (3-12) Transition metals	13	14	15	16	17
Strength	strong reducers	strong reducers	weak oxidizers	weak oxidizers or weak reducers	weak oxidizers or weak reducers	weak reducer or weak oxidizer	strong oxidizer or weak reducer	strong oxidizer



Identifying the properties of chemical elements according to place in the Periodic table

Example

Describe of the chemical element with the atomic number 15 by position in the periodic system of elements and the structure of the atom.

Solution

1. First, we find the chemical element #15 and write down its symbol and name. Chemical element number 15 is phosphorus. His symbol is P.

2. We characterize the position of the element (number of periods, group). Phosphorus is placed in the 3rd period and 15th group.

3. Let us give a general characteristic of the composition of the atom of a chemical element (nuclear charge, atomic mass, number of protons, neutrons, electrons and electron configuration).

The charge of the nucleus of the phosphorus atom is +15. The relative atomic mass of phosphorus is 31. The nucleus of the atom contains 15 protons and 16 neutrons (31-15 = 16). The phosphorus atom has three energy levels, on which there are 15 electrons.

Electron configuration: 15P: 1s2 2s2 2p6 3s2 3p3

4. We determine the maximum and minimum degree of oxidation of the phosphorus atom.

Phosphorus is the main group of the 15th group, therefore the maximum degree of oxidation of phosphorus +5. The minimum degree of oxidation for non-metals is in most cases equal to the difference between the group number and the number eight. So, the minimum degree of oxidation of phosphorus -3.

5. Determine the type of chemical element (metal or nonmetal, s-, p-, d- or f-element).

Phosphorus is a nonmetal. Since the last subshell in the phosphorus atom, which is filled with electrons, is the p-subshell, Phosphorus belongs to the family of p-elements.

6. We compose the formulas of higher oxide and phosphorus hydroxide and characterize their properties (basic, acidic or amphoteric).

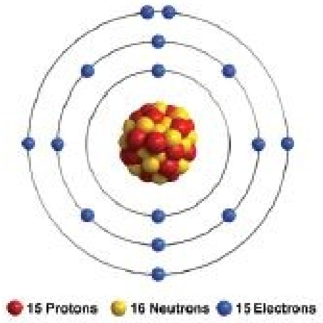
The highest phosphorus oxide, P2O5, exhibits the properties of an acid oxide. The hydroxide corresponding to the higher oxide, H3PO4, exhibits the properties of the acid. Let us confirm these properties by the equations of chemical reactions:

P2O5(s) + 3Na2O(s) = 2Na3PO4(s)

H3PO4(aq) + 3NaOH(aq) = Na3PO4(aq) + 3H2O(l)

7. Let's compare the non-metallic properties of phosphorus with the properties of the neighboring elements by period and group.

The neighbor of phosphorus in the subgroup is nitrogen. Neighbors of phosphorus over a period is silicon and sulfur. The non-metallic properties of the atoms of the chemical elements of the main groups increase with the increase in the ordinal number in the periods and decrease in the groups. Therefore, the nonmetallic properties of phosphorus are more shown than in silicon and less shown than in nitrogen and sulfur.



Atomic structure of phosphorus

White phosphorus

Research time

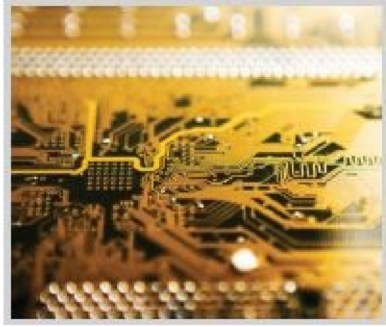
Write the chemical reactions of 3rd period elements with oxygen.

- Why are alkali metals very reactive?

- Why are passive metals does not react with oxygen?

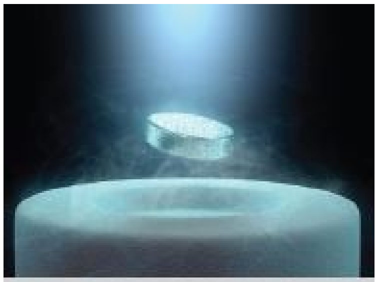
Chemfact

Interesting properties of gold 1 g of gold forms a sphere 37 mm the size of a small ball. It is so ductile that it can be drawn into a 20 μm thick and 165 m long, and so malleable that it can be hammered into a 1 m^2 sheet that is only 230 atoms (70 nm) thick!



Chemfact

Tl2Ba2Ca2Cu3O10 is a chemical formula of inner-metallic alloy that conduct electricity. At -1480C it becomes superconductor (see photo)



Terminology

- periodicity - периодтылық / периодичность;
- violently - шабытты / бурно;
- to behave - солай көрсетеді / вести себя;
- reducer - тотықсыздандырғыш / восстановитель;
- oxidizer - тотықтырғыш / окислитель.

Literacy

1. Identify the element that fits each description.

a. an alkaline earth metal in period 3

b. a transition metal in period 4, group 8

c. a main group element in period 3, group 17

d. a main group element in period 3, group 2

e. a halogen in period 3

f. an inner transition metal with three 5f electron

2. What element is located in group 1 but is not an alkali metal?

3. Name two elements in the periodic table that have chemical properties similar to phosphorus.

4. Name two elements in the periodic table that have chemical properties similar to magnesium.

5. Rank the following elements in order of decreasing reducing property: calcium, silicon, oxygen, magnesium, and carbon.

6. Rank the following elements in order of increasing oxidizing property: nitrogen, fluorine, magnesium, sodium, and phosphorus.

QUESTIONS AND PROBLEMS

1. What is periodic trend?

2. How does electronegativity changes in a group and in a period?

3. How does atomic radii changes in a group?

4. How does ionization energy changes in a period?

5. How does electron affinity changes in a group?

6. How does acidic properties changes in a period?

7. How does basic properties changes in a group?

8. How does metallic properties changes in a group?

9. How does nonmetallic properties changes in a period?

10. How does oxidizing properties changes in a group?

11. How does reducing properties changes in a period?

12. Which atom of the 3Li and 19K would have the higher first ionization energy?

13. Which atoms in the 11Na-16S and 4Be-5B pairs would have the higher first ionization energy?

14. Compare the metallic properties of the following elements; 19K, 11Na, 12Mg and 6C

15. Among the neutral atoms 7N, 8O, 11Na and 12Mg, which one has the greatest atomic radius?

16. Among the elements (2He, 10Ne, 18Ar, 36Kr, 54Xe and 86Rn) which one has the greatest atomic radius?

17. Are there any elements whose first ionization energy is smaller than its second ionization energy? Explain

18. Among the elements, 20Ca, 15P and 17Cl, which one has the lowest first ionization energy?

19. Compare the elements 4Be, 5B, 7N and 8O in terms of their first ionization energies.

20. Arrange the elements, 9F, 10Ne and 11Na in decreasing order of their first ionization energies.

21. Compare the elements 10Ne, 11Na and 17Cl in terms of their second ionization energies

22. Which elements have highest second ionization energies in a period? Explain

23. From which of these isoelectronic elements 9F-, 11Na+ and 12Mg2+ is it more difficult to give an electron?

24. Why is the first ionization energy of an element of group 2 higher than that of an element of group 13 in a period? Explain.

25. Why is the first ionization energy of 19K lower than that of 20Ca, but the second ionization energy of K higher than that of Ca?

26. What is the electronegativity? Explain.

27. Compare atomic radii of the following elements: Al, Cl, P, Si, S.

28. Compare atomic radii of the following elements: Mg, Ba, Sr, Be, Ca, Ra.

29. Compare electronegativity values of the following elements:

C, F, O, N, Be.

30. By considering the electronegativity values, arrange the following bonds with respect to their ionic character.

I. Si–H II. C–Cl III. C–O IV. Al–C V. Si–C

31. What is the most active metal in the 4th period?

32. What is the most active nonmetal in the 3rd period?

33. Compare electron affinity of the following elements: Cs, Rb, Na, K, Li.

34. State whether the oxides of the elements 6C, 14Si, 16S, and 20Ca with oxygen (CO, CO2, CaO, SiO2, SO2 and SO3) are acidic or basic.

35. What is an amphoteric oxide?

36. Which of the following oxides is/are amphoteric:

BaO, Al2O3, N2O5, K2O, ZnO, MgO.

37. Analyze the changes in the value of nuclear charges, atomic radii, electronegativities and degrees of oxidation of the 4th period. What are the patterns of these changes in periodic table - in the group from top to bottom or from left to right? How does the metallic properties of the elements and the nature of their oxides and hydroxides change in this direction?

38. Compose formulas for manganese oxides and hydroxides. How does the acid-base and oxidation-reduction character of these compounds change? Are these compounds subject to a general pattern of changes in the properties of oxides and hydroxides?

39. Which two oxides of the followings are the most basic:

BaO, K2O, TiO2, CaO, Al2O3, MgO, ZnO.

Specify the valence electrons of the selected elements.

3 CHAPTER

CHEMICAL BONDS

CHAPTER 3: CHEMICAL BONDS

3.1 CHEMICAL BONDS

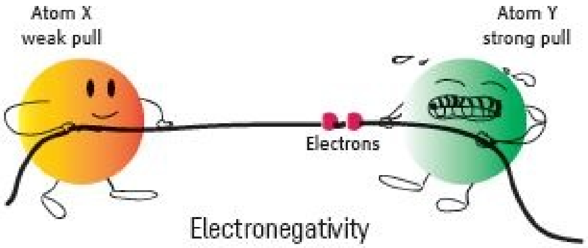
How can you tell the order of increasing boiling points based on the strength of bonds between atoms?

You will:

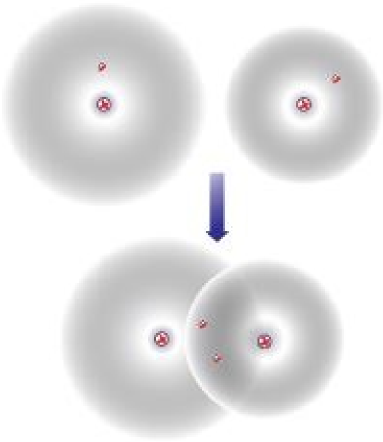
- explain the properties of covalent and ionic bond;
- explain the formation of covalent bonds by the exchange and donor-acceptor mechanisms;
- explain the formation of double and triple bonds;
- understand the electronegativity concept;
- write Lewis dot structure of elements and ions.

Electronegativity

Suppose molecule of a XY molecule is forming between atoms of X and Y. As they approach each other, positively charged nucleus of Y attracts electrons of X. At the same time, nucleus of X attracts electron of Y. However, the repulsion between atoms is taking place as well. You can think of stable state of a molecule as minimum energy state resulting from nucleus-nucleus repulsion and nuclei-electrons attraction. Chemical bond is a connection between atoms in a compound. As we mentioned earlier nuclei-electrons attraction is what holds atoms together in a molecule. Each atom has different attracting power for electrons in a compound. This ability of attracting electrons is called electronegativity. That is to say, in a molecule of XY, each atom attracts electrons differently. Sometimes an atom with high electronegativity value may even take an electron from neighbouring atom, which has lower electronegativity value by forming ions.

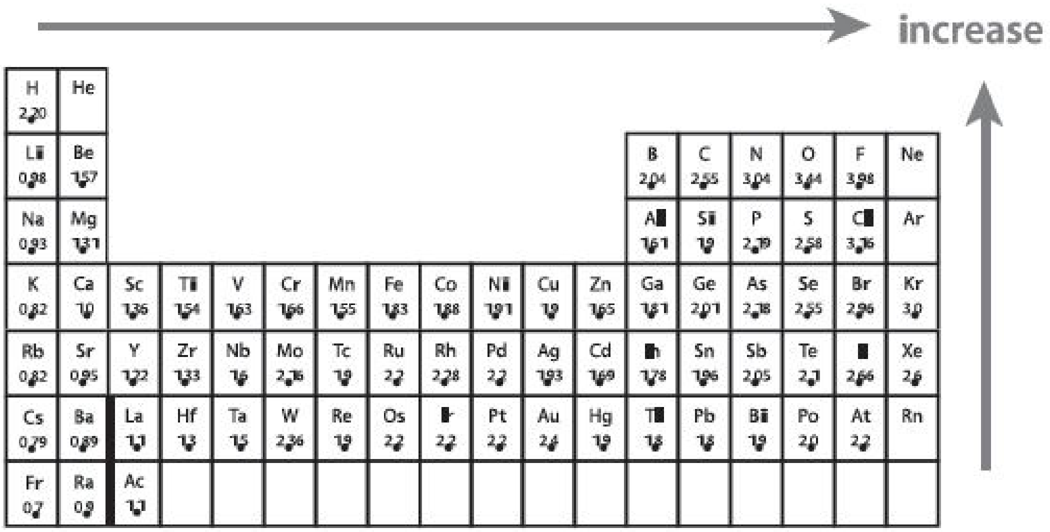


Electronegativity



Formation of covalent bonding

Electronegativity depends on atomic radius and charge of an atom. It does not have a unit. One of the widely used electronegativity scale is made by Linus Pauling. He made this scale by using bond dissociation energies. The maximum value is assigned to fluorine (4.0), and the minimum value is assigned to francium (0.7). The electronegativity values increase from bottom to top and from left to right across the periodic table.



Lewis structures

Gilbert Lewis proposed an idea of writing elements with their valence electrons, because difference in valence electrons of atoms gives them different chemical properties. The electrons are written as dots around a symbol of an element. Some elements with their Lewis dot representations are given below.

H_1: $1s^1$
He_2: $1s^2$
N_7: $1s^22s^22p^3$

O_8: $1s^22s^22p^4$
F_9: $1s^22s^22p^5$
Ne_{10}: $1s^22s^22p^6$

When you write Lewis structure for nitrogen, place 2s2 electrons in one of the four sides of the symbol. Other electrons that are located in the 2p3 orbitals are written on different sides, as each electron is located in different p orbitals (2px, 2py, and 2pz).

Ionic Bond

Whenever a chemical reaction takes place between elements, the elements in the new molecule have different electron configuration (or amount of electrons) than its elemental form.

For example, sodium in its elemental form contains 11 electrons. However, in table salt, it is present in cationic form Na+, which has 10 electrons.

Let us study how sodium and chlorine atoms form sodium chloride. Sodium and chlorine have electronegativity values of 0.9 and 3.0 respectively. As they approach each other, chlorine starts to draw the electron cloud from sodium because of its high electron pulling power. In the end, it takes one electron of sodium to make chloride anion and sodium cation (finally forming sodium chloride). In sodium chloride, sodium gains neon's electron configuration by giving an electron to chlorine. At the same time, chlorine gains electron configuration of argon by accepting an electron. They both have electron configurations of noble gases.

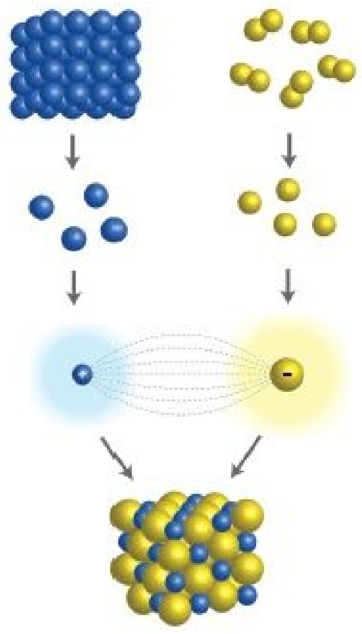
When you write Lewis structure for nitrogen, place 2s2 electrons in one of the four sides of the symbol. Other electrons that are located in he 2p3 orbitals are written on different sides, as each electron is located in different p orbitals (2px, 2py, and 2pz).

In general, atoms in compounds tend to have noble gas configuration to become stable. That is why ions of certain elements have different charges in their compounds. Aluminium has to lose 3 electrons to gain electron configuration of neon (Al3+) , and oxygen has to take 2 more electrons to gain electron configuration of neon (O2-). You may have noticed that all noble gases have valence electron configuration of ns2np6. Hence, sodium and chlorine also gains this valence electron configuration in table salt. This rule is called an octet rule. It states that main group elements tend to have 8 electrons in their valence shell when they form a compound. However, hydrogen and some elements located in the of 2nd period can have helium's valence shell electron configuration (a duplet, 1s2).

The formation of sodium chloride is an example of an ionic bond formation. Ionic bond is a chemical bond that occurs when electron transfer occurs between elements. Usually, electron transfer takes places between a metal and a non-metal, and both of them tend to gain electron configuration of noble gases. In addition, ionic compound has less energy than broadly diffused elements in their atomic form. Thus, table salt is more stable than diffused atoms of sodium and chlorine.

Below, electron configurations of some elements with their corresponding ions are given. Notice that, when they form ions they have the same number of electrons as noble gases.

Na_{11}: $1s^2 2s^2 2p^6 3s^1$	$Na_{10}{}^{1+}$: $1s^2 2s^2 2p^6$
K_{19}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$K_{18}{}^{1+}$: $1s^2 2s^2 2p^6 3s^2 3p^6$
Mg_{12}: $1s^2 2s^2 2p^6 3s^2$	$Mg_{10}{}^{2+}$: $1s^2 2s^2 2p^6$
Cl_{17}: $1s^2 2s^2 2p^6 3s^2 3p^5$	$Cl_{18}{}^{1-}$: $1s^2 2s^2 2p^6 3s^2 3p^6$
O_8: $1s^2 2s^2 2p^4$	$O_{10}{}^{2-}$: $1s^2 2s^2 2p^6$

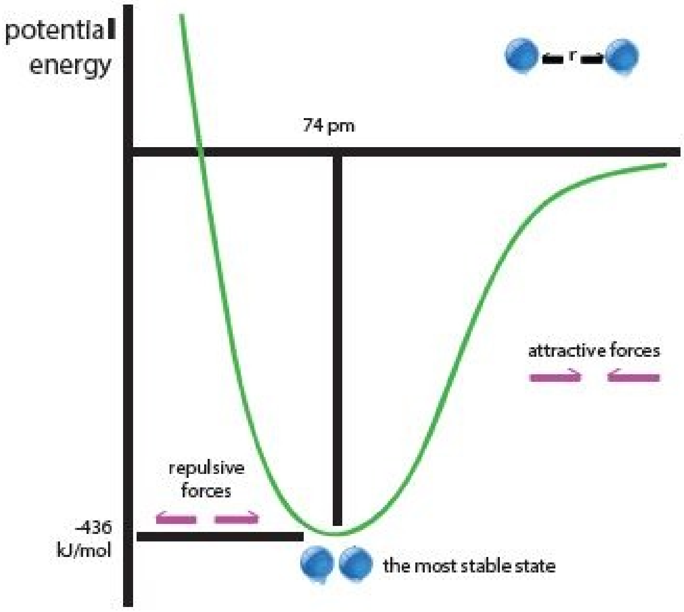


Formation of ionic bond

Covalent bond

If two atoms have large difference in electronegativity, one of them tend to pull and take electron(s) from the other. What happens if one of them doesn't have enough pulling power to remove an electron? How two hydrogen atoms form a hydrogen molecule, as they both have the same value of electronegativity?

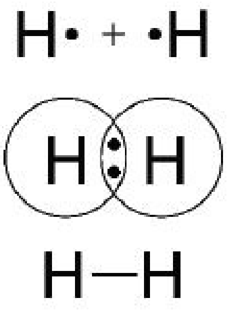
Covalent bond is a chemical bond, where electrons are shared between atoms. In this type of bonding, electrons that form a chemical bond are attracted to both nuclei. Let's take a hydrogen molecule as an example. When two hydrogen atoms approach each other, each of hydrogen atoms' nuclei attract another hydrogen atom's electron. When this attraction and repulsion between two nuclei reaches a minimum, covalent bond forms. This distance of minimum energy is called a bond distance or a bond length. They cannot get closer than the bond distance as the repulsive force between nuclei dominates, and they start to repel each other.



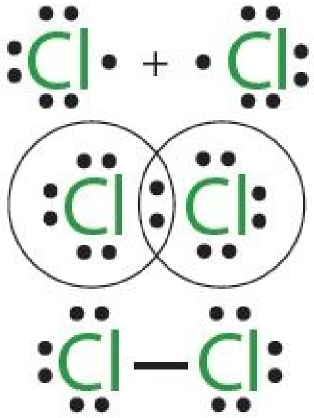
By taking into account the octet rule and the concept of sharing, in hydrogen molecule, each hydrogen is in the stable state as they both have 2 electrons (helium's duplet). When representing a hydrogen molecule, shared electrons are placed in between hydrogen atoms. Two shared electrons form one covalent bond; a line is used to represent a covalent bond.

It is possible for more than two electrons to be shared in a covalent bond. In case of an oxygen molecule, each oxygen needs two electrons to fulfil their valence shell. In order to get neon’s electron configuration they share 4 electrons to become O2. Each oxygen contributes 2 electrons for this double bond to form. As you can see, two lines are placed between two oxygen atoms, and each line represents one bond.

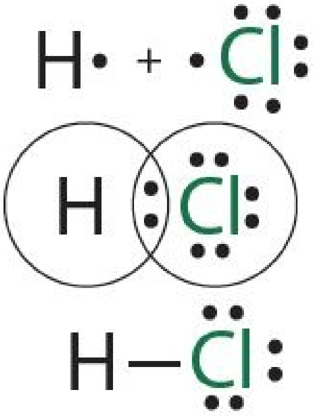
In nitrogen molecule, triple bond is what holds two nitrogen atoms together. The length of these bonds are in order of triple bond < double bond < single bond. One of the reason why nitrogen is so unreactive is that it has a strong triple bond, which requires a lot of energy to break. In some compounds like BeCl2, BH3 and PCl5 atoms or Be, B and P do not follow the octet rule. In BeCl2 and BCl3, beryllium and boron have an incomplete octet (6 electrons), while P has an expanded valance shell (10 valence electrons).



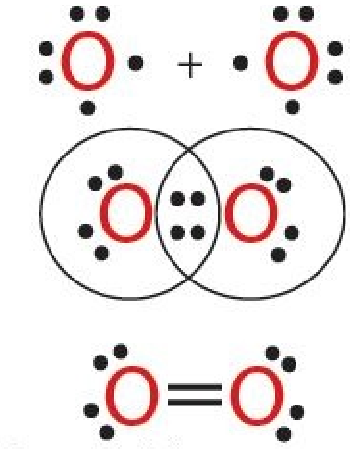
Hydrogen molecule, Lewis representation



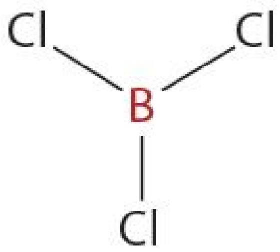
Chlorine molecule, Lewis representation

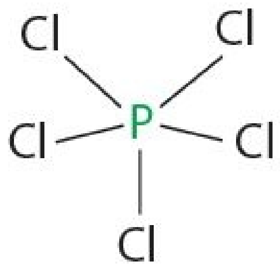


HCl molecule, Lewis representation.



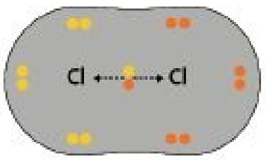
Oxygen molecule, Lewis representation.





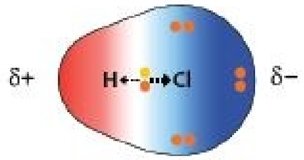
In hydrogen molecule, two atoms forming a covalent bond have the same value of electronegativity. That is to say, they pull the shared electrons equally. A nonpolar covalent bond is a covalent bond where electrons are shared equally. When covalent bond is formed between two different atoms, due to the difference in electronegativity value, the electrons are shared unequally. Thus, resulting in partial negative charge on the atom which have a higher electronegativity, and partial positive charge on an atom which have a lower electronegativity. This type of covalent bond is called a polar covalent bond.

(a)



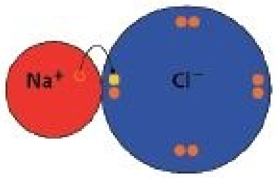
Nonpolar covalent bond

(b)



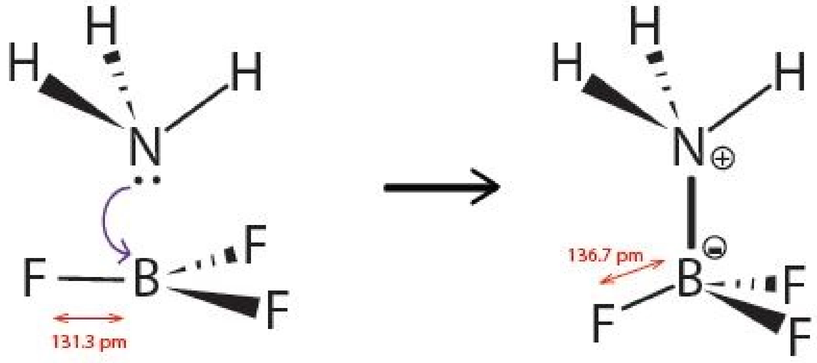
Polar covalent bond

(c)



Ionic bond

Sometimes a pair of electrons that form a covalent bond can be donated by one substance. A coordinate covalent bond, sometimes termed as a dative bond is formed in this way. In the formation of NH3BF3, a pair of electrons is provided by ammonia.



Formation of coordination covalent bond

Chemistry around us

Cans are often made of tin (steel covered with a tin layer). Familiar to us on bronze products and pewter, tin is also used in the composition of tin soldiers.

Research time

Open in browser Phet. Atomic Interactions. Research why do noble gases does not react with other elements in room condition.

Chemfact

One of the theories about the death of the composer Mozart is that he was poisoned due to an overdose of "medical" antimony.

Activity

Write a description of determining chemical structures of the compounds. Use the internet to help you. Include the following information:

- scientific methods

- scientific instruments

Research time

Open in browser Phet. Molecule polarity. Research how molecules polarized in electric field.

Literacy

1. Explain the bond formation in O_2 and N_2 using orbital representation. ($_8O$, $_7N$)

2. Draw the molecular structures of the following species. Are these molecules polar or nonpolar?

SiH_4, NH_3, CH_4, H_2O, HF, PH_3, CO_2, PCl_3, BeH_2, OF_2

3. Explain the bonding in the NH_4^+ and BF_4^- ions.

4. Draw the electron dot structures of the following elements: $_8O$, $_{19}K$, $_{15}P$, $_{20}Ca$

5. Show the formation of ionic bonds between Li and Cl , Ba and I, Li and O

Terminology

- corresponding - сәйкес келетін / соответствующий;
- to expand - ұлғаю / расширять.

3.2 HYBRIDIZATION OF ORBITALS

Why is the H-O-H bond angle in a water molecule H2O smaller than the H-C-H bond angles in methane CH4?

You will:

- explain types of hybridization;
- explain the relationship of the structure and properties of substances

Hybridization

The mixing of different orbitals, which are closer in energy levels, to form new orbitals with the same energy level is called hybridization. The new orbitals formed at this new energy level are called hybrid orbitals.

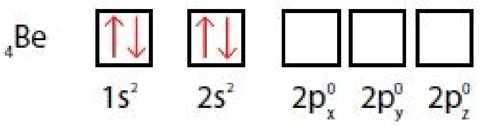
Hybridization occurs between two or more different types of orbitals (generally s, p or d orbitals). For example, there are three types of hybrid orbitals which may occur between the s and p orbitals, these are named as sp, sp2 and sp3 hybrid orbitals. It is not possible to form hybrid orbitals between the same type of orbital. For example s orbitals cannot form ss hybrid orbitals and p orbitals cannot form pp hybrid orbitals. Group 2 elements of the periodic table can undergo sp hybridization, Group 3 elements can undergo sp2 hybridization and Group 4 elements can undergo sp3 hybridization. Molecules formed by atoms of these groups generally contain bonds with hybridized orbitals. Since hybrid orbitals overlap with each other, stable molecules are formed. Maximum overlapping often occurs between the hybrid orbital of one atom and the orbital of another atom, molecules formed in this way have lower energies. The energy needed for hybridization is balanced against the energy which is released during bond formation.

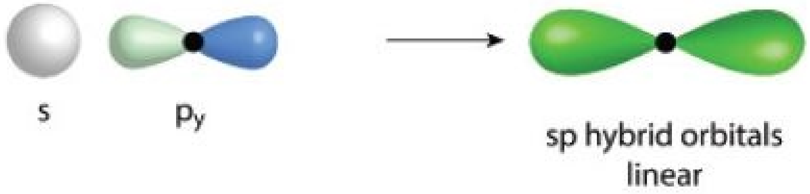
Hybridization occurs during the formation of a chemical bond. It is not possible to occur in an individual atom. Hybrid orbitals play an important role in determining the geometric shape of a molecule. Now let's study sp, sp2 and sp3 hybridization in detail.

sp hybridization

Let's look at the ground state electron configuration and orbital diagram of the beryllium atom (4Be) which is the first element in group 2.

As it does not have any unshared electrons, beryllium would not be expected to form a covalent bond. But experimentally it is found that beryllium is able to form two covalent bonds. To form these bonds one electron moves from the 2s orbital to the 2p orbital leaving the atom in an excited state with two unpaired electrons

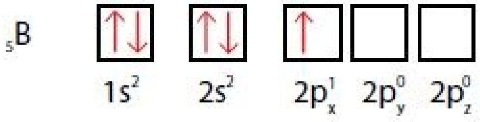


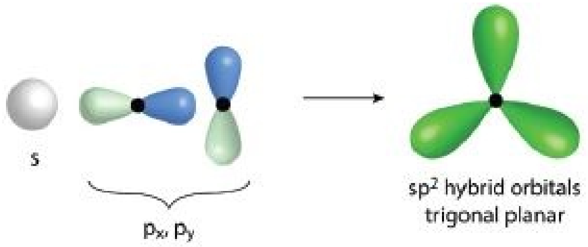


Two sp hybrid orbitals are formed as a result of mixing one s orbital with one p orbital. The energy of the sp hybrid orbitals is greater than the s orbital but less than the p orbitals. Each sp orbital has 50% s character and 50% p character.

sp2 hybridization

Let's look at the ground state electron configuration and orbital diagram of Boron (5B) which is the first element of group 3. It is found experimentally that boron can form three covalent bonds. But as it has only one unpaired valence electron in the ground state, it appears only to be able to form one bond. To create three unpaired electrons, one electron in the 2s orbital is promoted to the 2py orbital. To form three identical bonds with the same energy, two p and one s orbitals mix to give three sp2 orbitals. These three identical and half filled sp2 orbitals enable boron to form three identical bonds.



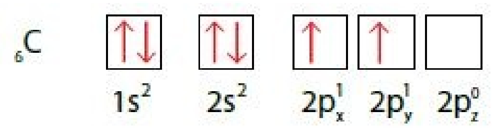


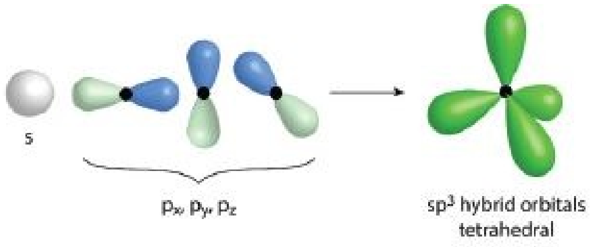
Three sp2 hybrid orbitals are formed as a result of mixing one s orbital with two p orbitals. Each sp hybrid orbital has 33.3% s and 66,7% p character.

sp3 hybridization

Let's look at the ground state electron configuration and orbital diagram of carbon (6C) which is the first element in group 4.

In this case since carbon has only two unpaired electrons, it seems likely that it will only form only two covalent bonds, but it is known that carbon can form four covalent bonds. To form four bonds, one electron is promoted from the 2s orbital to the 2pz orbital. Then the one 2s orbital and three 2p orbitals mix together to form four new sp3 hybrid orbitals as shown in figure. So in this case of hybridization, three p and one s orbital combine to give four identical sp3 orbitals. The carbon atom can also undergo sp2 and sp hybridization. Later we will study the sp and sp2 hybridization of carbon when it forms double and triple bonds.





Four sp3 hybrid orbitals are formed as a result of mixing one s orbital with three p orbitals. Each sp3 hybrid orbital has 25% s and 75% p character.

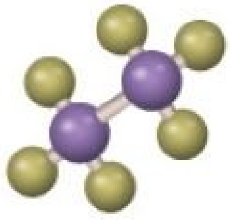
Research time

Open in browser Phet. Molecule Shapes.

Compare shapes and structures of different molecules.

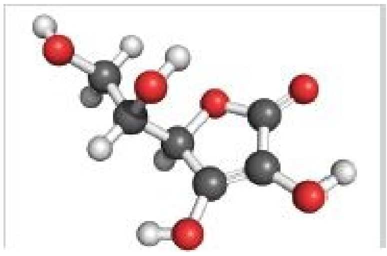
What is the reason that atomic orbitals hybridize?

Why do atoms undergo hybridization before forming a bond?



Chemfact

British chemist Walter Haworth first determine chemical structures of vitamin C (also known as ascorbic acid) and carbohydrates. And received the Nobel prize for Chemistry for his work.



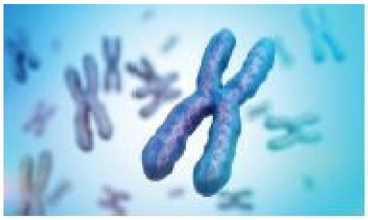
Activity

German scientists Schleiden, Virchow and Bütschli discovered the structure of the human chromosomes.

Write the short text about the human chromosomes. Include the following information:

- chemical elements in the human chromosomes

- genetic information in the human chromosomes



Literacy

1. Show the hybridization of the calcium atom when it bonds with fluorine. 20Ca, 9F

2. Show the hybridization of the phosphorus atom when it bonds with hydrogen. 15P, 1H

3. Show the hybridization of the boron atom when it bonds with chlorine. 5B, 17Cl

4. Explain the bond structure of the CH2Cl2 molecule by using electron dot structure.

5. Explain the bond structure of the N2H4, C2H2 molecules by using electron dot structure. (6C, 1H, 7N)

Terminology

- hybridization - гибридтену / гибридизация;
- to promote - дамыту / продвигать

3.3 VSEPR THEORY

Why is the water molecule bent? Why aren't the 2 hydrogen atoms on a plane, exactly 180 degrees apart?

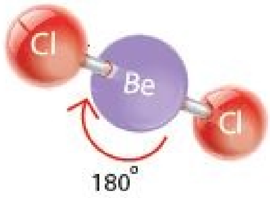
You will:

- use the VSEPR theory of electron pairs to predict the spatial shape of molecules and ions.

When writing formulas of covalently bonded compounds, we do not show how they arranged in three-dimensional space. One way of showing molecular shape of compounds is to use valence shell electron repulsion model (VSEPR).

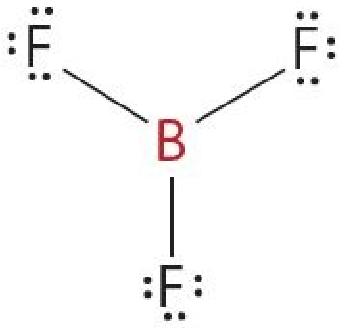
It will be easier to start with molecules, which have only one central atom. In these types of molecules, lone pairs and shared electrons of the central atom repel each other, and tend to be in the state when they have minimum repulsion. Let’s take BeCl2 as an example. In these types of molecules two atoms of Cl tend to be in a state with minimum repulsion. It is achieved when two atoms are located at 180° to each other. This shape is called a linear shape, and BeCl2 is a linear molecule.

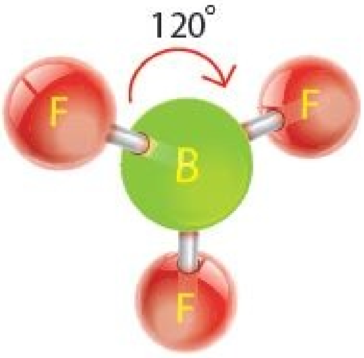
Cl : Be : Cl



Shape of $BeCl_2$ molecule.

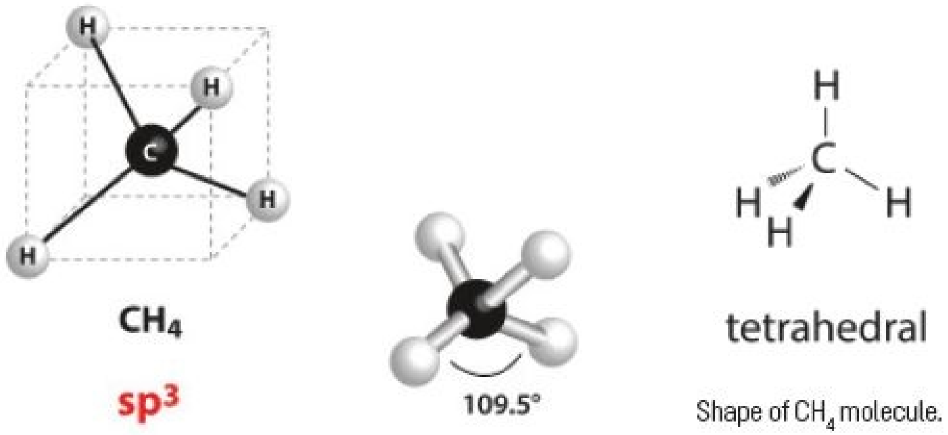
In BF3 three fluorine atoms minimize the repulsion by locating themselves at 120° to each other. This arrangement is called a trigonal planar geometry.





Note that BeCl2 and BF3 do not follow the octet rule.

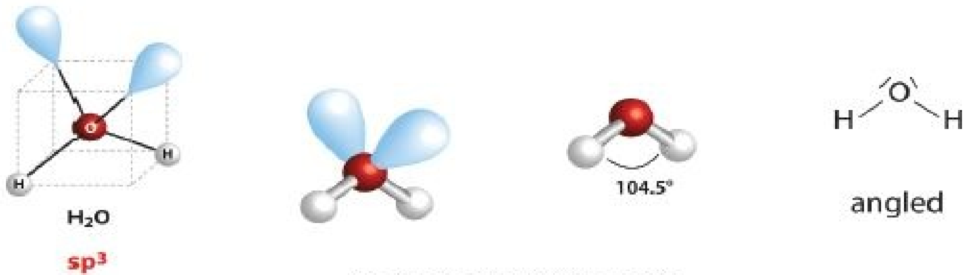
The methane molecule (CH4) turns out to have a tetrahedral geometry, where each hydrogen atom is located at 109.5° to each other.



Shape of CH_4 molecule.

You might expect linear geometry for H2O molecule as it has only two hydrogen atoms to oxygen atom. However, there are two additional lone pairs also present in H2O molecule, which also repel each other and bonding electrons of H. The repulsion of lone pairs are stronger than repulsions between bonding electrons. That is due to the fact that lone pairs take more volume (they are more diff used) compared to bonding electrons, thus, they repel each other more strongly than bonding electrons. The order or repulsion strength is:

Lone pair - lone pair > lone pair - bonding electrons > bonding electrons - bonding electrons

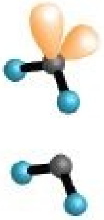
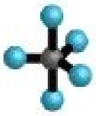
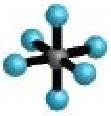


Bend geometry of H_2O molecule

This arrangement is named a bend geometry. Due to the presence of lone pairs which repel bonding electrons more strongly, the angle between two hydrogen atoms is slightly less than tetrahedral geometry.

The electron arrangement is tetrahedral in shape, but the molecular shape is said to be bent. When we classify molecular shape we omit lone pairs. However, in electron arrangement of a molecule both lone pair and bonding electrons have to be taken into account. In addition the angle between two hydrogen atoms in water molecule is slightly less than 109.5^{o}.

The general procedure for finding the geometry of the molecule is given in the picture number.

CN	number of lone electron pairs							
	0	**e.g.**	**1**	**e.g.**	**2**	**e.g.**	**3**	**e.g.**
2	 linear	CO_2						
3	 trigonal planar	BCl_3 SO_3	 angled	SO_2 NO_2^- O_3	 linear	CO		
4	 tetrahedral	CH_4 SO_4^{2-}	 trigonal pyramidal	NH_3	 angled	H_2O	 linear	HCl
5	 trigonal bipyramidal	PCl_5	 bisphenoidal (seesaw)	SF_4	 T-shaped	ClF_3	 linear	I_3^-
6	 octahedral	SF_6	 square pyramidal	ClF_5	 square planar	ICl_4^-		
7	 pentagonal bipyramidal	IF_7						

Molecule geometries by VSEPR model

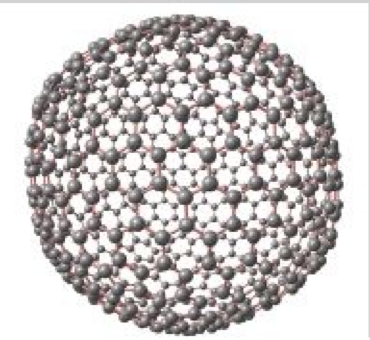
Research time

Open in browser Phet. Molecule Shapes.

Compare shapes and structures of different molecules.

Chemfact

In 1985, Robert Curl and Harold Kroto received the Nobel Prize for the discovery of the fullerene C60. Fullerene is one of the allotrope of carbon that producing from graphite by using laser rays technology.



Literacy

1. Determine the molecular geometry of following compounds:

CH2I2, ClF3, H2S, SO3, SO2

2. Use VSEPR theory to determine the shapes of each of the following.

a. SCl2 b. PF3

c. NCl_3 d. NH_4^+

3. Use VSEPR theory to predict the geometry of the PCl_3 molecule.

4. Using VSEPR theory predict the shape (molecular geometry) of $COCl_2$ and is it polar or nonpolar.

Terminology

- bend - майысқан, бүктелген / изгиб;
- bipyramidal - бипирамидалық / бипирамидальный.

3.4 INTERMOLECULAR BONDS

Why can lizard glue itself on the wall but not on the water?

You will:

- understand the mechanism of hydrogen bonding;
- predict the properties of compounds with different types of bonds and types of crystal lattices;
- explain the nature of intermolecular interactions;
- explain the nature of the metallic bond and its effect on the physical properties of metals.

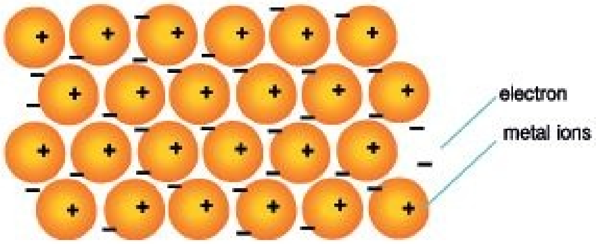
All gases condense at low temperatures to become liquids. If the temperature is lowered still further, liquids turn into solids. In the solid and liquid phases, molecules are very close to each other. This is because forces hold the molecules together in the solid and liquid states. We have already studied intramolecular bonds within molecules in the previous chapter. In this chapter, we will examine the forces of attraction between the particles in liquids and solids. These forces affect the boiling point, melting point, hardness, and electrical and heat conductivity of a substance. In this chapter, we will study metals, ionic solids, network solids, dipole-dipole attractions, van der Waals forces and hydrogen bonds.

Metallic bond

Metal atoms have a small number of valence electrons. The nuclear attractive forces between the metal nuclei and their valence electrons are reduced by the inner electrons (which are closer to nucleus). Thus, the nucleus of a metal atom exerts only a small attractive force on its valence electrons and these electrons are able to move more freely. For this reason, metal atoms have very low ionization energies and electronegativities.

Metals are solid at room temperature, except for mercury. This tells us that the attractive forces between metal atoms are strong. The valence electrons of metal atoms can easily move from the free orbitals of one atom to another. These electrons that can move freely between atoms form an "electron sea". An attractive force occurs between the negatively charged "sea of electrons" and the positively charged nuclei. Metal atoms are held together because of this attractive force. This is called the metallic bond.

Iridium is a hard, brittle, lustrous, dense, transition metal



Because of the attraction between the electron sea and the positively charged sodium nuclei, a metallic bond is formed. Because of these freely moving electrons in the electron sea, metals are good conductors of heat and electricity. They can be drawn into wires and can be hammered into shape easily. In the periodic table, metallic bond strength generally decreases as you go down a group.

However across a period, the metallic bond strength generally increases from left to right. This is because the metals on the right hand side possess a higher number of valence electrons. Let us compare the metallic bonds of sodium, magnesium and aluminum. sodium (11Na) has one valence electron, magnesium (12Mg) has two and aluminum (13Al) three valence electrons. The metallic bonding in Al is the strongest, and the weakest in Na.

Strong metallic bonds increase the boiling point, melting point, and the hardness of the metal. Sodium, magnesium and aluminum melt at 98°C, 650°C and 660°C respectively.

Ionic solids

When metal and nonmetal atoms come together they form ionic bonds, as you will remember from the previous chapter. In the ionic bond, the metal atoms which lose electrons become positively charged and the nonmetal atoms, which gain electrons, become negatively charged. Electrostatic attraction occurs between the positive and negative charges, holding the ions together. These electrostatic attractions act in all directions. Thus, ionic crystalline solids consist of metal ions are surrounded by non-metal ions and non-metal ions surrounded by metal ions. Therefore, ionic solids do not have a molecular structure.

As the attraction between the ions is strong, the melting and boiling points of ionic solids are very high. For example, NaCl melts at 801°C. In ionic solids, electrons are held in place around the ions so they don't conduct electricity. However, in aqueous solution and molten state, they do conduct electricity. Electrical conductance of ionic compounds is not due to movement of electrons but to the movement of ions.

Ionic compounds are brittle but not ductile, as is shown in picture (right). When they are hammered, their structure is disturbed, the hammered part shift s and similar charged ions repel each other and the ionic substance breaks down into smaller pieces. Since movement of the ions disturbs the balance of electrical charge, ionic solids cannot be drawn into wires and are broken easily.

Ionic solids are brittle and can not be drawn into wires or hammered into plates. As the ionic bonds are very strong, compounds containig such bonds ar very stable.

Network solids

In molecular covalent compounds, intermolecular forces are very weak in comparison with intramolecular forces. For this reason, most covalent substances with a low molecular mass are gaseous at room temperature. Others, with higher molecular masses may be liquids or solids, though with relatively low melting and boiling points. However, in some covalent substances, known as network solids, atoms are bonded together in a way that forms a network structure.

Diamond

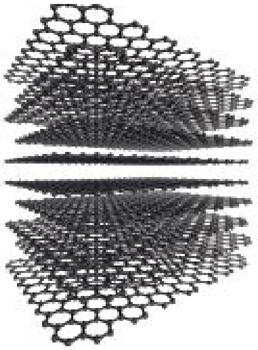
The most typical example of a network solid is diamond. In diamond each carbon atom is covalently bonded to four other carbon atoms forming a tetrahedral shape (The type of hybridization that corresponds to this tetrahedral structure is sp3). This structure is extremely strong and this makes diamond the hardest natural substance.

Silicon carbide SiC is another network solid. Silicon carbide is used as an abrasive because of its hard structure.

Diamond and silicon carbide are nonconductors of electricity and have very high melting points. The melting point of diamond is about 3500°C and that of SiC 2830°C.

Graphite

In graphite, a different form of carbon, atoms are bonded to each other in such a way that a hexagonal structure is formed in a plane. Each carbon atom is bonded to three other carbon atoms with an angle of 120° between the bonds. The bonding involves sp2-sp2 hybrid overlap and this gives rise to layers. Bonds in the same plane are very strong, but attractions between the layers are much weaker. Because of this weak bonding between the layers, the layers can slide over each other. This makes graphite a good lubricant, and gives it a soft feel. It conducts electricity.



Van der Waals forces

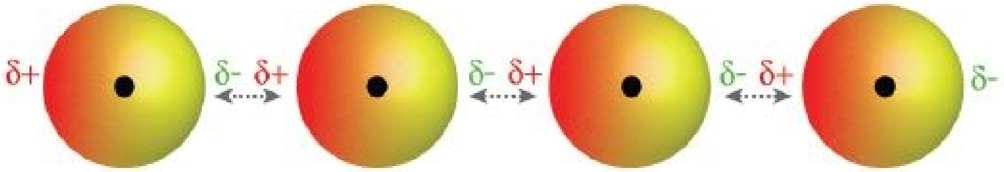
Noble gases and non-polar molecules such as CO2 and CH4 do not have dipoles. In these molecules, the movement of electrons results in nonpolar molecules becoming temporarily polar; an instantaneous dipole is formed. The molecule which becomes momentarily polar then causes its neighboring molecule to become polar. Thus a weak attraction occurs between the molecules. This attraction is named the van der Waals force.

Van der Waals forces depend upon the electron density of the atoms. Increasing number of atoms in a molecule increases the van der Waals attractive force. Since the electron number of a neutral atom is equal to its proton number, atoms which have a large proton number have strong van der Waals forces between their molecules. Therefore, van der Waals forces are stronger between molecules with high molecular masses.

Van der Waals forces between I2 molecules are stronger than those between Cl2 molecules because clearly, iodine has bigger molecules than chlorine. Propane (C3H8) is bigger than methane (CH4), so the Van der Waals forces between C3H8 molecules are stronger than those between CH4 molecules. For small molecules, the Van der Waals force is weaker than dipole-dipole forces and hydrogen bonding. Thus, small nonpolar molecules have low melting and boiling points.

Let’s compare the intermolecular forces between I2 and Cl2. I2 has the greater molecular mass so the Van der Waals forces between its molecules are greater in comparison with Cl2. Therefore at room temperature iodine is solid whereas chlorine is gas.

Formation of Van der Waals forces. Molecules approaching each other gain momentarily polar character. The container contains bromine

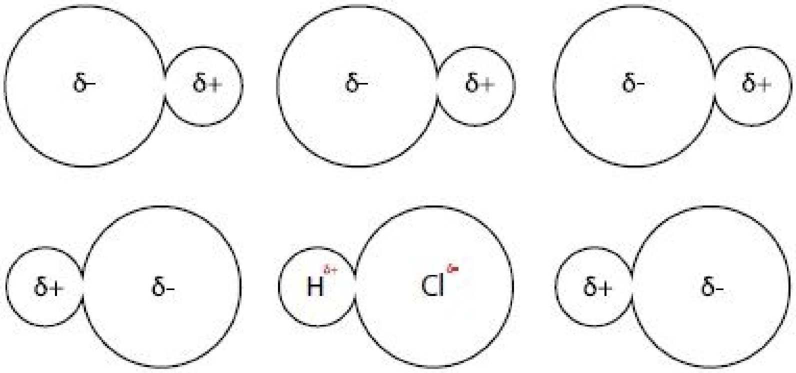


Van der Waals interaction: included dipole caused by charge fluctuations

Dipole-dipole forces

In polar covalent substances, the molecules have partial positive and negative charges because of the electronegativity differences between the atoms. The molecules are said to possess a dipole. There is an attraction between the positive end of one dipole and the negative ends of neighboring dipoles. This attraction is called dipole-dipole attraction.

For example, in the HCl molecule, the partial charge on the hydrogen atom is positive and the partial charge on the chlorine atom is negative. Between neighboring HCl molecules there is an attraction between the hydrogen and chlorine ends of the molecules. Dipole-dipole forces between HCl molecules are much weaker than the covalent bond within the molecule.

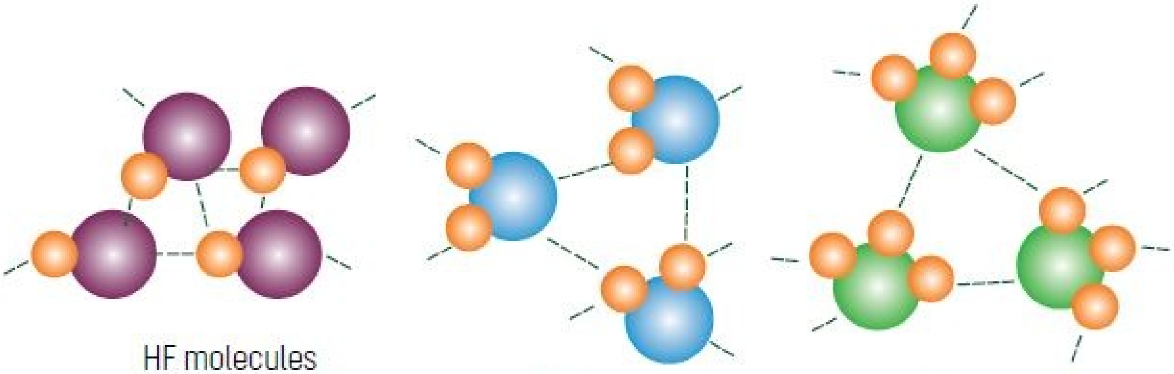


Formation of dipole-dipole forces

Hydrogen bonds

Fluorine, oxygen and nitrogen are the most electronegative elements. Therefore the compounds that these elements form with hydrogen (HF, H2O,NH3) are highly polar. Due to this polarity an intermolecular force that is much stronger than the usual dipole-dipole attraction occurs. These strong intermolecular forces are called hydrogen bonds.

A hydrogen bond is formed between a hydrogen atom and a lone pair electrons from an atom in a neighboring molecule. For example, the hydrogen atom of a water molecule forms a hydrogen bond with the lone pair of electrons from an oxygen atom in another water molecule.



HF molecules

H_2O molecules

NH_3 molecules

Although there are van der Waals forces between water molecules, the effect of the hydrogen bonding is much stronger than that of the van der Waals forces. For this reason, the boiling point of water is higher than expected. If the boiling point of a substance is high, this tells us that the intermolecular forces in this substance are also high.

The boiling points of the hydrides of the group 14 elements (CH4, SiH4 and SnH4) increase gradually with increasing atomic number. Other groups (15, 16 and 17) show the same general trend, however, NH3, H2O and HF show an unexpected increase in boiling point. This is explained by the fact that these molecules have hydrogen bonding occurring between them. The boiling points don't show the expected pattern.

For example, if the curve that takes in H2Te, H2Se, H2S is extended to the second period; the boiling point of water would be expected to be around –90°C. However, the boiling point of water is 100°C and so it can be summarized that hydrogen bonding increases the boiling point of water by around 190°C.

Research time

Open in browser Ptable. Choose the tab "Properties".

Compare the conductivity, melting and boiling points, hardness and densities of metals.

Research time

Open in browser Mohs scale of mineral hardness. Compare the harness of natural minerals.

What makes the diamond the hardest mineral?

What is the hardest substance on Earth other than a diamond?

Activity

In the movie "Blood Diamond" (2006) shows the difficulties of diamond mining in Africa. Write a short text describing diamond mining. Use the internet and movies to help you. Include the following information:

- how to mine diamond
- how much is the price of a diamond
- which methods are used in the process

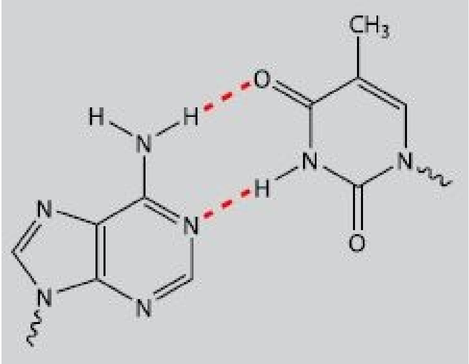
Chemfact

Van der Waals interactions allow the gecko lizard to walk straight up a wall.

Chemfact

DNA contains four bases: Guanine, Cytosine, Adenine, and Thymine.

The complementary base pairs of guanine with cytosine and adenine with thymine connect to one another using hydrogen bonds.



Chemistry around us

Attraction between a hydrogen and an electronegative atom is called a hydrogen bond. In living cells, the electronegative partners are usually oxygen or nitrogen atoms.

Literacy

1. Compare the ionic character of the following salts: KF, KCl, KBr and KI

2. Explain whether or not the following substances conduct electricity:

Al(s), KCl(aq), Hg(l), $NaNO_3$(s), SiC(s), LiF(aq)

3. What is the main type of bonding that must be overcome to carry out the changes of state given below?

- Fe(s) → Fe(l);

- H_2O(l) → H_2O(g);

- I_2(s) → I_2(l);

- $AlCl_3$(s) → $AlCl_3$(l);

- S_8(s) → S_8(l).

4. Arrange the alkali metals according to their metallic bond strength.

5. Which of the following substances have only van der Waals forces between their molecules?

a. Ne; b. CH_4; c. O_3; d. $MgCl_2$; e. CO_2; f. CO; g. Na_2O.

Terminology

- intermolecular - молекулааралық / межмолекулярные;
- crystal lattice - кристалдық тор / кристаллическая решетка;
- inner electrons - ішкі электрондар / внутренние электроны;
- dipole-dipole forces - диполь-дипольдық күштер / диполь-дипольные силы;
- instantaneous - лезде, жылдам / мгновенный.

Table 6 *Average Bond Energies (kj/mol)*

	Bond	Energy	Bond	Energy	Bond	Energy	Bond	Energy
Single Bonds								
	H–H	432	N–H	391	Si–H	323	S–H	347
	H–F	565	N–N	160	Si–Si	226	S–S	266
	H–Cl	427	N–P	209	Si–O	368	S–F	327
	H–Br	363	N–O	201	Si–S	226	S–Cl	271
	H–I	295	N–F	272	Si–F	565	S–Br	218
			N–Cl	200	Si–Cl	381	S–I	~170
	C–H	413	N–Br	243	Si–Br	310		
	C–C	347	N–I	159	Si–I	234	F–F	159
	C–Si	301					F–Cl	193
	C–N	305	O–H	467	P–H	320	F–Br	212
	C–O	358	O–P	351	P–Si	213	F–I	263
	C–P	264	O–O	204	P–P	200	Cl–Cl	243
	C–S	259	O–S	265	P–F	490	Cl–Br	215
	C–F	453	O–F	190	P–Cl	331	Cl–I	208
	C–Cl	339	O–Cl	203	P–Br	272	Br–Br	193
	C–Br	276	O–Br	234	P–I	184	Br–I	175
	C–I	216	O–I	234			I–I	151
Multiple Bonds								
	C=Cl	614	N=N	418	C≡C	839	N≡N	945
	C=N	615	N=O	607	C≡N	891		
	C=O	745 (799 in CO_2)	O_2	498	C≡O	1070		

Table 7 *Average Bond Lengths (pm)*

	Bond	Length	Bond	Length	Bond	Length	Bond	Length
Single Bonds								
	H–H	74	N–H	101	Si–H	148	S–H	134
	H–F	92	N–N	146	Si–Si	234	S–P	210
	H–Cl	127	N–P	177	Si–O	161	S–S	204
	H–Br	141	N–O	144	Si–S	210	S–F	158
	H–I	161	N–S	168	Si–N	172	S–Cl	201
			N–F	139	Si–F	156	S–Br	225
			N–Cl	191	Si–Cl	204	S–I	234
	C–H	109	N–Br	214	Si–Br	216		
	C–C	154	N–I	222	Si–I	240	F–F	143
	C–Si	186					F–Cl	166
	C–N	147	O–H	96	P–H	142	F–Br	178
	C–O	143	O–P	160	P–Si	227	F–I	187
	C–P	187	O–O	148	P–P	221	Cl–Cl	199
	C–S	181	O–S	151	P–F	156	Cl–Br	214
	C–F	133	O–F	142	P–Cl	204	Cl–I	243
	C–Cl	177	O–Cl	164	P–Br	222	Br–Br	228
	C–Br	194	O–Br	172	P–I	243	Br–I	248
	C–I	213	O–I	194			I–I	266
Multiple Bonds								
	C=C	134	N=N	122	C≡C	121	N≡N	110
	C=N	127	N=O	120	C≡N	115	N≡O	106
	C=O	123	O_2	121	C≡O	113		

QUESTIONS AND PROBLEMS

Covalent bond

1. Explain the bond formation in H_2 and N_2 using orbital representation. (1H, 7N)

2. Draw the molecular structures of the following species. Are these molecules polar or nonpolar?

SiH_4, NH_3, CH_4, H_2O, HF, PH_3, CO_2, PCl_3, BeH_2, OF_2

3. Define network covalent bonds; list four substances that have a network covalent structure.

4. The boiling points of silicon carbide SiC and silicon oxide SiO_2 are very high. Explain why this is so.

5. What are the differences in bonding between diamond and graphite?

6. Use a polar arrow to indicate the polarity of each bond: N-H, F-N, I-Cl.

Rank the following bonds in order of increasing polarity: H-C, H-O, H-N.

7. Define bond energy using the H-Br bond as an example. When this bond breaks, is energy absorbed or released?

Donor-acceptor mechanism

1.Explain coordinate covalent bonding and give one example.

2. Explain the bonding in the H_3O^+ and BF_4^- ions.

3. Show the coordinate covalent bond formed between BF_3 and NH_3 molecules?

The shape of the BF_3 molecule is trigonal planar but NH_3 molecule is trigonal pyramidal. Explain the reason for this difference.

Hybridization. Molecule geometry

1. Show the hybridization of the calcium atom when it bonds with fluorine. $_{20}Ca$, $_{9}F$

2. Show the hybridization of the magnesium atom when it bonds with chlorine. $_{12}Mg$, $_{17}Cl$

3. Show the hybridization of the boron atom when it bonds with hydrogen. $_{5}B$, $_{1}H$

4. Show the hybridization of the boron atom when it bonds with chlorine. $_{5}B$, $_{17}Cl$

5. Show the kinds of hybridization when the carbon atom bonds with chlorine. $_{6}C$, $_{17}Cl$

6. Show the kinds of hybridization when the carbon atom bonds with hydrogen. $_{6}C$, $_{1}H$

7. Explain the bond structure of the BH_3 molecule by using electron dot structure. ($_{5}B$, $_{1}H$)

8. Explain the bond structure of the C_2H_4, C_2H_2 molecules by using electron dot structure. ($_{6}C$, $_{1}H$)

9. Explain the bond structure of the $CHCl_3$ molecule by using electron dot structure.

Double, triple bond formation

1. Find the number of π and σ bonds in each of the following molecules.

O2, SiO2, N2, C2H4, C3H4

Electronegativity

1. Compare the electronegativities of the following elements F, Li, Na, O, P

2. Why do atoms tend to acquire a noble gas electron configuration?

3. Draw the electron dot structures of the following elements:

7N, 11Na, 15P, 20Ca, 35Br

4. Give the electron dot representations of the ions and compounds given below.

HBr, CO, CH4, PH3, NF3, F-, CO32-, S2-, NO3-

5. For the PH3 molecule, show its

- - Orbital representation.
- - Electron dot representation.
- - Line representation.

6. Both oxygen and polonium are members of group 16. Which is more metallic? Explain your answer in terms of atomic properties.

7. Which member of each pair is more metallic?

Li and Cs, Mg and Ba, N and Sb

8. Which member of each pair is less metallic?

S and Te, Be and Sr, Al and P

Ionic bond, ionic crystal networks

1. Which of the following compounds exhibit ionic bonding?

H_2O_2, H_2S, Li_2O, KCl, MgI_2, P_2O_5, P_2O_3

2. Compare the ionic character of the given compounds.

KCl, KF, MgO, FeS, NaF, CsCl

3. Show the formation of ionic bonds between

Na and Cl, Ca and I, Li and S

4. What is the difference between the formation of ionic and covalent bonds?

5. Describe the type of bonds in each of the following compounds.

$AlCl_3$, SF_6, $CHCl_3$, $Ba(NO_3)_2$, Na_2SO_4

6. Which of the compounds in the following pairs has the greatest ionic character?

CaF_2 and CaI_2, NaCl and KCl, KBr and KCl

7. Which forces are found in the following compounds?

LiBr, Na_2O, $SiCl_4$

8. Compare the following substances according to their electrical

conductivity? Give your reasoning.

- - sugar solution
- - table salt solution
- - vinegar
- - alcohol solution

9. When gaseous Na+ and Br- ions form gaseous NaBr ion pairs, 752 kJ/mol of energy is released. Why, then, does NaBr occur as a solid under ordinary conditions?

10. Use condensed electron configurations to depict the monatomic ions formed from each of the following atoms, and predict the formula of the compound the ions produce:

Ba and I, Sr and O, Al and Br, Cs and O

11. Identify the main group to which X belongs in each ionic compound formula:

XCl2, CaX, X2SO3

12. Identify the main group to which X belongs in each ionic compound formula:

X3PO4; X2(SO4)3; X(NO3)2

VSEPR theory

1. Determine the molecular geometry of following compounds:

CH2I2, ClF3, H2S, SO3, SO2

2. Use VSEPR theory to determine the shapes of each of the following.

a. SCl2 b. PF3 c. NCl3 d. NH4+

3. Use VSEPR theory to predict the geometry of the PCl3 molecule.

4. Using VSEPR theory predict the shape (molecular geometry) of COCl2 and is it polar or nonpolar.

Metalic bond, metallic crystal networks

1. Explain why alkali and alkaline earth metals melt at lower temperatures than transition metals?

2. Arrange the alkaline earth metals according to their metallic bond strength.

3. Arrange the given metals in order of increasing melting points.

3Li, 12Mg, 19K, 20Ca

4. How does each of the following atomic properties influence the metallic character of the main group elements in a period?

- Atomic radius
- Number of outer electrons
- Ionization energy

5. State the type of bonding: ionic, covalent, or metallic you would expect in each: LiCl(s), N2(g), K(s)

4 CHAPTER

STOICHIOMETRY

CHAPTER 4: STOICHIOMETRY

4.1 BASIC STOICHIOMETRIC LAWS OF CHEMISTRY

Will the mass of container change if the water inside the container evaporates?

You will:

- name and use fundamental stoichiometry laws in chemistry;
- explain the concepts of "relative atomic mass", "relative molecular mass", and "molar mass".

Stoichiometry

The basic laws of quantitative chemistry, including the laws of quantitative relationships between reacting substances using chemical reaction equations, the derivation of formulas of chemical compounds, constitute a branch of chemistry called stoichiometry.

The law of the conservation of mass

Mass conservation law is one of the basic laws in chemistry. It states that in any chemical reaction the sum of the masses of the reactants is equal to the sum of the masses of the products.

$$\Sigma m_{reactants} = \Sigma m_{products}$$

Let us give an example to understand this law better. Imagine a table with a bottle of KOH(aq), a bottle of MgCl2(aq), and a beaker standing on it. The mass of this table and its contents will not change even when some of the contents are mixed. As a result of the reaction, two new substances: Mg(OH)2 and KCl will appear in the beaker, but the total mass of the table and its contents will not change:

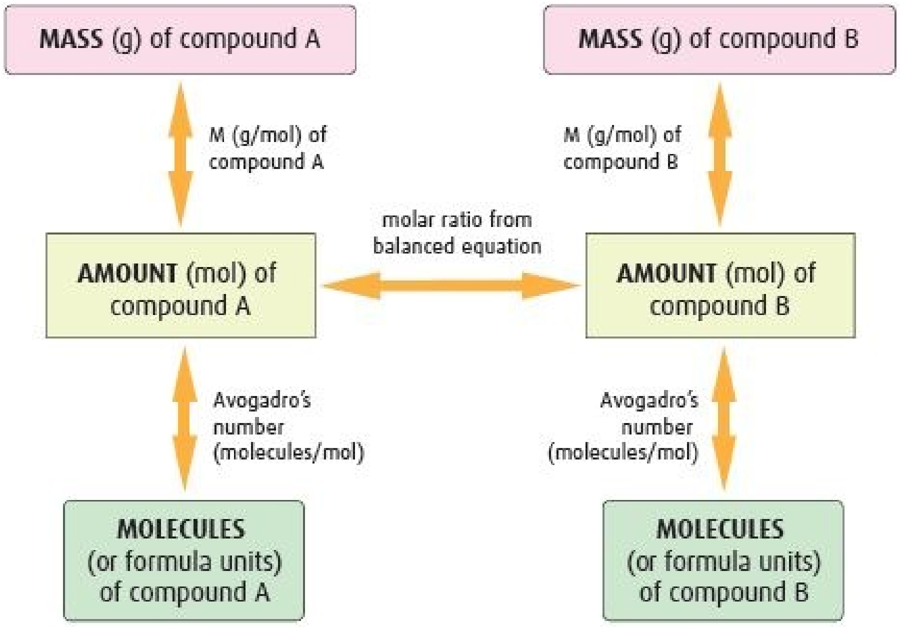
For example,

$$2KOH(aq) + MgCl_2(aq) = Mg(OH)_2(aq) + 2KCl(aq)$$

$$m(KOH) + m(MgCl_2) = m(Mg(OH)_2) + m(KCl)$$

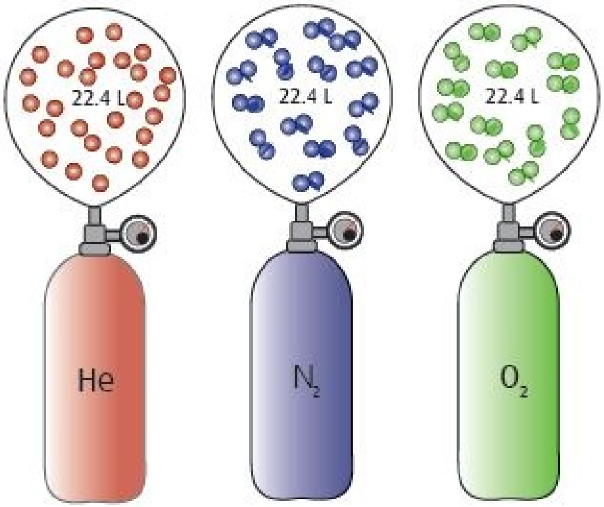
$$11.2\ g + 9.5\ g = 5.8\ g + 14.9\ g$$

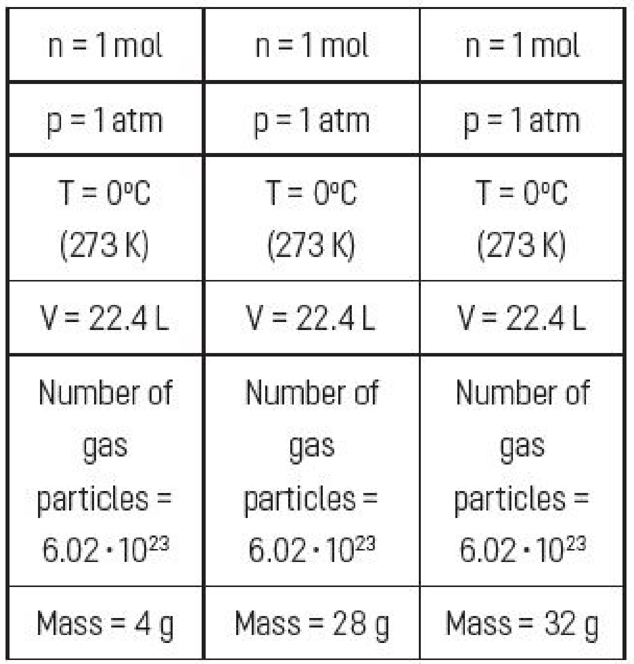
$$20.7\ g = 20.7\ g$$



Avogadro's law

Avogadro's law is the law according to which equal amounts of different gases, taken at the same conditions and contain the same number of molecules.





n = 1 mol	n = 1 mol	n = 1 mol
p = 1 atm	p = 1 atm	p = 1 atm
T = 0ºC (273 K)	T = 0ºC (273 K)	T = 0ºC (273 K)
V = 22.4 L	V = 22.4 L	V = 22.4 L
Number of gas particles = $6.02 \cdot 10^{23}$	Number of gas particles = $6.02 \cdot 10^{23}$	Number of gas particles = $6.02 \cdot 10^{23}$
Mass = 4 g	Mass = 28 g	Mass = 32 g

Avogadro’s law

Example

13.65L of methane gas reacts with oxygen to produce carbon dioxide and water vapor.

CH4(g) + 2O2(g) → CO2(g) + 2H2O(g)

Calculate volume of oxygen, carbon dioxide, and water vapor.

Solution:

The molar ratios are n(CH_4) : n(O_2) : n(CO_2) : n(H_2O) = 1 : 2 : 1 : 2

According to Avogadro's law the volume ratios will also be

V(CH_4) : V(O_2) : V(CO_2) : V(H_2O) = 1(13.65 L) : 2(13.65 L) : 1(13.65 L) : 2(13.65 L) = = 13.65 L : 27.3 L : 13.65 L : 27.3 L

Answer: V(CH_4) = V(CO_2) = 13.65 L V(O_2) = V(H_2O) = 27.3 L

The law of volume relations

This law states that at constant pressure and temperature the volumes of gases entering into a chemical reaction are in simple relations to each other and to the volumes of gaseous reaction products, that is, the ratio of the volumes in which the gases participate in the reaction correspond to the ratio of small integers.

This law reflects the fact that identical volumes of gases at the same temperature and pressure contain the same number of molecules (Avogadro's law).

For example, if 2 volumes of H_2 react with 1 volume of O_2 the product is 2 volumes of water vapor:

Two volumes of hydrogen + One volume of oxygen = Two volumes of water vapor

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Relative atomic mass and relative molecular mass

Elements come together in a certain mass ratio to form compounds. In order to compare these mass ratios, scientists choose 12C atom as a standard. The mass of the 12C isotope atom is accepted as 12.00 amu and other atomic masses of other elements were calculated accordingly. For example, hydrogen's atomic mass is equal to 1.008 (1 amu) and calcium's atomic mass is equal to 40.078 (40 amu) with respect to 12C that is 12 amu.

In other words, the relative atomic mass of an element is the average mass of its atom to 1/12 of the mass of a 12C atom. In the periodic table, the masses of atoms are written according to these relative calculations. For compounds; similar to relative atomic mass, a relative molecular mass is used. A relative molecular mass is the sum of relative atomic masses of the atoms found in a compound.

Keep in mind

The mass of reactants is equal to the mass of the reaction products.

Chemfact

In Chemistry stoichiometry calculations are based on the fact that atoms are conserved. They cannot be destroyed or created.

Research time

Calculate the molar volume of gases by using pV=nRT formula.

- p = 1atm, T=273 K,

- 1 mol gas,

- R- universal gas constant

Literacy

1. Some amount of methane gas reacts with 6.4 g of oxygen and the masses of the water and carbon dioxide produced are 3.6 g and 4.4 g respectively. Calculate the mass of methane gas reacted.

2. When 5.4 g of aluminum Al reacts with oxygen 10.2 g of aluminum oxide Al_2O_3 is formed. What is the mass of oxygen reacted?

3. 8.9 L of butane gas reacts with oxygen to produce carbon dioxide and water vapor.

$C_4H_{10}(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

Calculate volume of oxygen, carbon dioxide, and water vapor.

4. 42.8L of ammonia gas reacts with oxygen to produce nitrogen monooxide and water vapor.

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

Calculate volume of oxygen, nitrogen monooxide, and water vapor.

5. Calculate the relative molecular mass of SO_2 and KNO_3 .

6. Calculate the molecular formula mass of CO_2.

Terminology

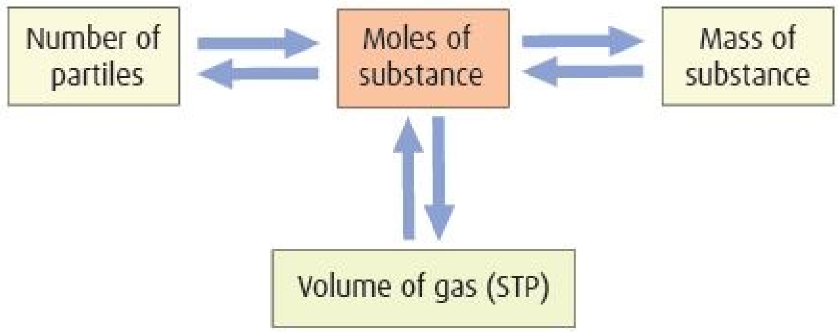
- stoichiometry - стехиометрия / стехиометрия;
- conservation - сақталу / сохранение;
- volume relation - көлемдік қатынас / объемное отношение.

4.2 MOLE CONCEPTION. MOLAR CONCENTRATION

Which gas is heavier 1 L of hydrogen or 1 L of methane and why? Give a reason.

You will:

- converting between amount of substance (in moles), mass (in grams), and number of chemical entities;
- solve problems with using concept of "molar concentration", "molar volume" at STP.



Use N as a unit factor: multiply by 1 mol / 6.02×1023

Use molar mass as a unit factor: multiply by 1 mol/g

Use molar volume as a unit factor: multiply by 1 mol/22.4 L

Example 1

Calculating the mass and number of atoms in a given number of moles of an element

a) Copper Cu metal is used to make coins. How many grams of Cu are in 0.045 mol of Cu?

b) Iron Fe the main component of cast iron, is the most important metal in industry. How many Fe atoms are in 600 g of iron sample?

Solution

a) We know the number of moles of copper (0.045 mol) and have to find the mass. To convert moles of Cu to grams of Cu, we multiply by the molar mass of Cu, which we find in the Periodic table.

Converting from moles of Cu to grams:

Mass of Cu = n(Cu) • Mr(Cu) = 0.045 mol • 64 g/mol = 2.88 g Cu

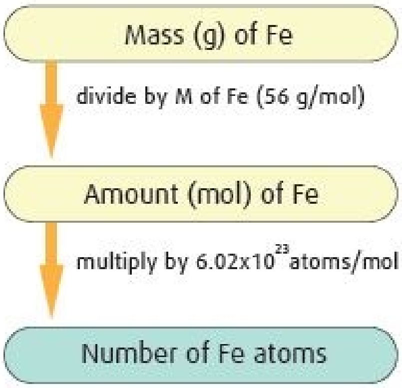
b) We know the grams of iron (600 g) and need the number of Fe atoms. We cannot convert directly from grams to atoms, so we first convert to moles by dividing grams of Fe by its molar mass. Then, we multiply number of moles by Avogadro's number to find number of atoms.

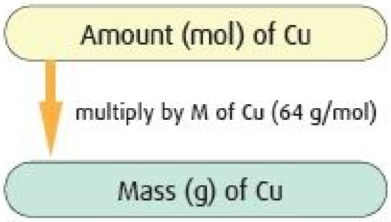
Converting from moles of Fe to grams:

Moles of Fe = m(Fe) / Mr(Fe) = 600 g / 56 g/mol = 10.71 mol Fe

Converting from moles of Fe to number of atoms:

Number of Fe atoms = n(Fe) • NA = 10.71 • 6.02•1023 = 6.447·1024 atoms





Copper coins

Example 2

Calculating molar volume of gases

0.26 moles of hydrogen sulfide H2S gas will occupy how many liters at STP?

Solution

We know the number of moles of H2S gas and have to find volume. To convert moles of H2S to liters of H2S, we multiply by the standard volume at STP.

Converting from moles of H2S to liters:

Volume of H2S = Molar volume at STP multiply by amount (mol) of H2S:

V = n(H2S) • VSTP = 0.26 mol • 22.4 L/mol = 5.824 L H2S

Molar concentration (Molarity)

The concentration of a solution expressed as the amount of solute dissolved in a given amount of solution:

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \quad \text{or} \quad M = \frac{\text{mol solute}}{\text{L soln}}$$

Different molarities of solutions

Example 3

Acetic acid C2H4O2 is the simplest carbonic acid. What is the molarity of an aqueous solution that contains 86 g of acetic acid in 640 mL?

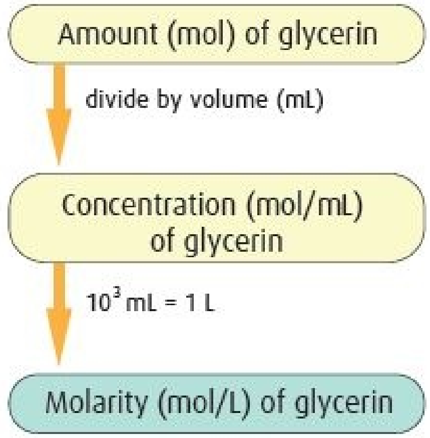
Solution

The molarity is the number of moles of solute in each liter of solution. We are given the gram and volume (640 mL), so we convert the mass to moles and divide moles by volume and convert the volume to liters to find the molar concentration.

Converting from grams of C2H4O2 to moles:

Moles of C2H4O2 = m(C2H4O2) / Mr(C2H4O2) = 86 g / (24 + 4 + 32) g/mol = 1.43 mol of C2H4O2

Molarity = (1.43 mol of C2H4O2) • 1000 mL / 640 mL = 2.234 M C2H4O2 (or 2.234 mol/L C2H4O2)



Literacy

1. How many moles of silver are in 2.8•1021 atoms of silver?

2. How many molecules are there in 2.7 moles of potassium phosphate K3PO4 ?

3. Find the mass, in grams, of 5.6•1024 molecules of FeS2.

4. Calculate the volume occupied by 1.16 kg of CO2 gas at STP.

5. What is the mass of butane C4H10 in a 20 L container of the gas at STP?

6. What is the molarity of an aqueous solution that contains 23 g of potassium permanganate $KMnO_4$ in 500 mL?

7. How many moles of NaCl are in 240 mL of 0.63 M NaCl?

Chemfact

Heaviest metal in the Earth is iridium Ir (d = 22.65 g/cm3). A ball of this metal with a radius 10 cm you can not even tear off the floor!

Chemfact

The heaviest gaseous compound at room temperature is colorless tungsten fluoride WF_6 (d =12.9 g/L).

Terminology

- interconverting - бір түрден екінші түрге айналу / взаимопревращение;
- molarity - молярлық / молярность.

4.3 PERCENT PURITY OF SUBSTANCES. LIMITING REAGENTS

How is metals extracted and purified before it can be useful to us?

You will:

- solve amount of products of a reaction by using known amount of reactants, if one of the reactants is in excess/limiting amount;
- solve amount of products of a reaction by using percent purity of reactants.

Example 1

Calculating Amounts of Reactant and Product in a Limiting-Reactant Problem

How many grams of solid aluminum sulfide can be prepared by the reaction of 30.0 g of aluminum and 15.0 g of sulfur? How much of the non limiting reactant is in excess?

Solution

First we write the balanced equation. Because the amounts of two reactants are given, we know this is a limiting-reactant problem. To determine which reactant is limiting, we calculate the mass of aluminum sulfide Al2S3 formed from each reactant assuming an excess of the other. We convert the grams of each reactant to moles and use the appropriate molar ratio to find the moles of Al2S3 each forms. Whichever yields less Al2S3 is the limiting reactant. Then we convert this lower number of moles of Al2S3 to mass. The roadmap shows the steps.

Writing the balanced equation:

$$2Al(s) + 3S(s) \rightarrow Al2S3(s)$$

Step 1. Finding the moles of Al2S3 from the moles of Al (if Al is limiting):

Moles of Al = m(Al) / Mr(Al) = 30 g / 27 g/mol = 1.111 mol Al

Moles of Al2S3 = mole of Al / 2 = 1.111 mol / 2 = 0.556 mol Al2S3

Step 2. Finding the moles of Al2S3 from the moles of S (if S is limiting):

Moles of S = m(S) / Mr(S) = 15 g / 32 g/mol = 0.469 mol S

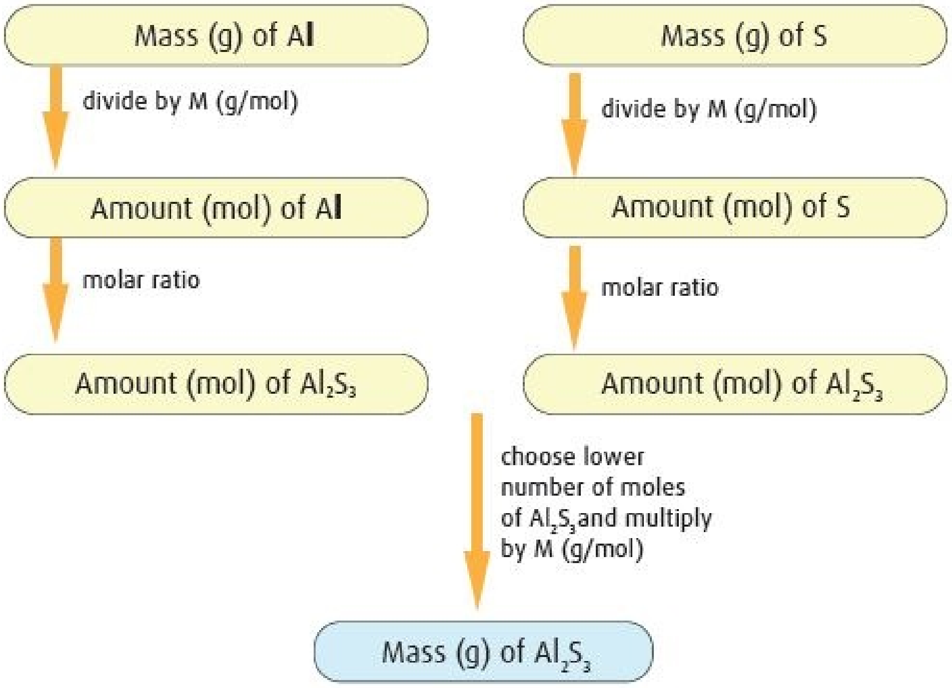
Moles of Al2S3 = mole of S / 3 = 0.469 mol / 3 = 0.156 mol Al2S3

Step 3. Thus, S is the limiting reactant because it yields fewer moles of Al2S3:

$0.156 \text{ mol} < 0.556 \text{ mol}$

Step 4. Converting from moles of Al2S3 to grams:

Mass (g) of Al2S3 = n(Al2S3) · Mr(Al2S3) = 0.156 mol · (27·2 + 32·3) = 23.4 g Al2S3



Example 2

Percent purity of reactants

Chalk is almost pure calcium carbonate CaCO3. 15 g of chalk is put into excess hydrochloric acid solution and the volume of carbon dioxide CO2 gas produced found to be 2.912 L at STP. What was the percentage of calcium carbonate in the original sample?

Solution

Writing the balanced equation:

CaCO3(s) + 2HCl(aq) → CaCl2(aq) + H2O(l) + CO2(g)

Step 1. Finding the moles of produced carbon dioxide gas:

Moles of CO2 = V(CO2) / VSTP = 2.912 L / 22.4 L / mol = 0.13 mol CO2

Step 2. Converting from moles of CO2 to moles of CaCO3: The molar ratio is 1 mol

CaCO3/1 mol CO2, so

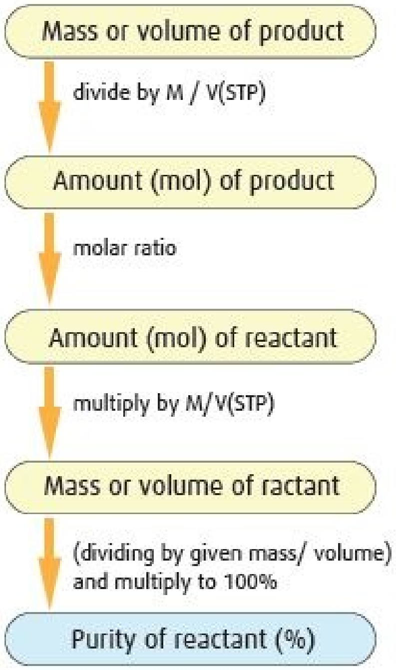
Moles of CaCO3 = moles of CO2 = 0.13 mol CaCO3

Step 3. Converting from moles of CaCO3 to grams:

Mass(g) of CaCO3 = n(CaCO3) · Mr(CaCO3) = 0.13 mol · 100 g/mol = 13 g CaCO3

Step 4. Calculating the percent purity:

% purity of CaCO3 = (13 g / 15 g) · 100% = 86.67%



Polymetal ore

Pure lead

Chemistry around us

Percent purity of copper and gold in their ores are 50 g and 10 g respectively in 1 ton of ores.

Literacy

1. How many moles of lithium oxide can be produced from the reaction of 6 mol of lithium and 3 mol of oxygen gas?

2. Ammonia is used in the production of many chemicals, such as fertilizers, explosives, polymers and detergents. Calculate the mole number of ammonia that can be synthesized from the reaction of 4 mol of nitrogen with 6 mol of hydrogen.

3. When sodium is heated with sulfur, sodium sulfide is produced. What mass of sodium sulfide can be formed by heating 12.8 g of sulfur with 9.2 g of sodium?

4. When an unknown quanity of magnesium is reacted with HCI, 4.48 L of H2 at STP together with some magnesium chloride are formed.

- a. What mass of magnesium chloride is formed?
- b. If the sample of magnesium is 96 % pure, what mass of magnesium sample is used in the reaction?
- c. What mass of HCI solution that is 20 % HCI by mass would it be required to produce 4.48 L of H2 at STP?

5. When 20 g of iron is reacted with oxygen. 20 g of iron (III) oxide is formed. What percent of iron is reacted with oxygen? (Hint: 20 g iron (III) oxide → ? mol iron (III) oxide → ? mol Fe → Fe → ? % of Fe)

6. How many grams of sodium chloride that is 90% pure are required to produce 73 g of HCI according to the reaction below?

NaCI(aq) + H2SO4(aq) → NaHSO4(aq) + HCI(aq)

Chemfact

Gold is a very passive metal. But it reacts with ozone gas to for gold ozonide; it reacts with fluorine and bromine, chlorine, iodine solutions to form gold halides. Gold also dissolves in “King’s water”, concentrated selenic acid and alkali metal cyanides.

Activity

Write the description of purity of a minerals. Find out more using the internet. Include the following information:

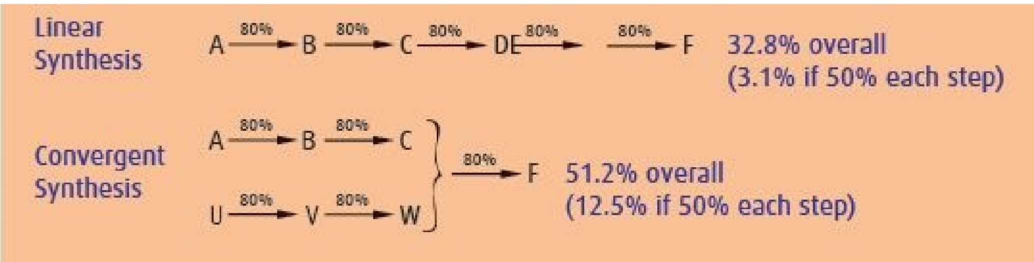
- which minerals important in the Earth’s crust?
- how to mine minerals
- which minerals are very expensive?

Terminology

- extract - бөліп алу / извлечение;
- purify - тазарту / очистить;
- limit-excess - жетіспеушілік-артық қалу / недостаток-избыток

4.4 YIELD OF CHEMICAL REACTION

A yield of final products in multistep reactions (A → B → C → D → E → ...) is extremely low. How to explain this mathematically?



You will:

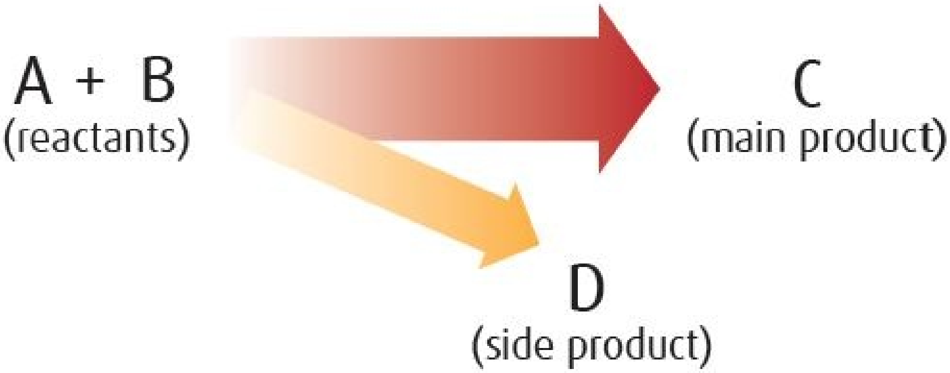
- calculate product yield in percent form.

The percent yield is used to relate the amount of product that is actually obtained (the practical amount) to the theoretical amount. Until now, we have assumed that as a result of a chemical reaction, the reagents are completely converted into products according to stoichiometric calculations. In practice, this happens rarely. For example, in the preparation of a substance in the form of a precipitate on the displacement reaction in solution, some of it is still dissolved (there are no substances absolutely insoluble).

The theoretical mass (mtheor) is the mass that is found by the reaction equation, provided that the reagents are completely converted into products.

Actual mass is a mass that is obtained in practice (mpract). It is clear that the practical mass is less than theoretical equal to it. To estimate the completeness of the chemical process uses the notion of product output, as well as losses in production. The output of the product (signified by the letter η) is equal to the ratio of practical and theoretical masses, expressed in fractions of a unit or percentages:

$$\%\ \text{Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \text{x}100\%$$



The effect of side reactions on yield. One reason the theoretical yield is never obtained is that other reactions lead some of the reactants along side paths to form undesired productsю

Example 1

Marble (calcium carbonate) reacts with hydrochloric acid solution to form calcium chloride solution, water, and carbon dioxide. What is the percent yield of carbon dioxide if 3.8 g of the gas is collected when 10 g of marble reacts?

Solution

We are given the actual yield of CO_2 (3.8 g), so we need the theoretical yield to calculate the percent yield. After writing the balanced equation, we convert the given mass of calcium carbonate (10 g) to amount (mol). We use the molar ratio to find the amount of CO_2 formed and convert that amount to mass (g) to obtain the theoretical yield. Then, we use yield equation to find the percent yield (see the roadmap).

Writing the balanced equation:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Step 1

Converting from grams of calcium carbonate to moles:

Moles of $CaCO_3$ = 10 g $CaCO_3$ / (40 + 12 + 48) g/mol = 0.1 mol $CaCO_3$

Step 2

Converting from moles of $CaCO_3$ to moles of CO_2: The molar ratio is 1 mol CO_2/1 mol $CaCO_3$, so

Moles of $CaCO_3$ = moles of CO_2 = 0.1 mol CO_2

Step 3

Converting from moles of CO_2 to grams:

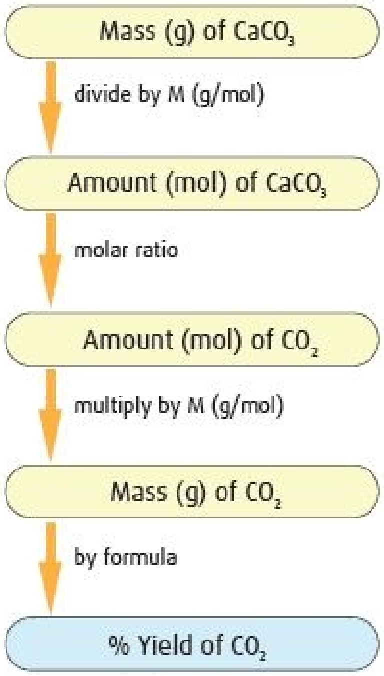
Mass (g) of CO_2 = $n(CO_2) \cdot M(CO_2)$ = 0.1 mol • 44 g/mol = 4.4 g of CO_2

Step 4

Calculating the percent yield:

$$\%\ \text{yield of } CO_2 = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \text{x}100\% = 3.8\ \text{g} \times 100\% / 4.4\ \text{g} = 86.36\%$$

Natural marble



Example 2

When heated, the nitrates of alkali metals decompose to give nitrites of the metals and oxygen gas. Calculate the volume of oxygen gas (at STP) produced from the decomposition of 62 g of sodium nitrate. The yield of the reaction is 92 %.

Solution

We know that sodium nitrate decomposes to give sodium nitrite and oxygen gas:

2NaNO3(s) → 2NaNO2(s) + O2(g)

Step 1

Converting from grams of NaNO3 to moles:

n(NaNO3) = 62 g NaNO3 / (23 + 14 + 48) g/mol = 0.73 mol NaNO3

Step 2

Converting from moles of NaNO3 to moles of O2: The molar ratio is 1 mol O2 / 2 mol NaNO3, so

2 moles of NaNO3 = 1 moles of O2

n(O2) = 0.73 / 2 = 0.365 mol O2

Step 3

Converting from moles of O2 to liters:

Volume (L) of O2 = n(O2) • VSTP = 0.365 mol • 22.4 L/mol = 8.176 L of O2

Step 4

8.176 L is the theoretical volume of O2

$$\%\ \text{Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \text{x} 100\%$$

Calculating actual volume of O2 gas:

Vactual = yield • Vtheor / 100% = 8.176 L • 92% / 100% = 7.522 L of O2 gas

Literacy

1. A sample of magnesium carbonate is heated and the mass of magnesium oxide produced found to be 80 g. Calculate the mass of decomposed magnesium carbonate if the yield of the reaction is 80%.

2. Oxygen gas can be obtained from the decomposition of potassium chlorate, $KClO_3$. In a laboratory experiment, the decomposition of 2.45 g of potassium chlorate produces 0.48 g of oxygen. Calculate the percent yield of this reaction.

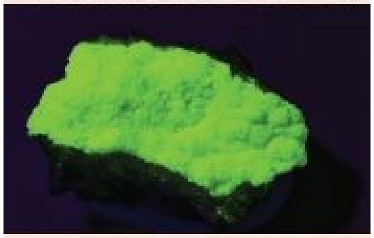
3. What is the percent yield if 121.5 g of silver is produced when 13.5 g of aluminum is reacted with excess silver nitrate solution. The unbalanced reaction equation is

$Al(s) + AgNO_3(aq) \rightarrow Al(NO_3)_3(aq) + Ag(s)$

4. What is the percent yield if 27 g of H_2O are obtained when 33 g of C_3H_8 reacts with 56 L of O_2 at STP. The second product of the reaction is carbon dioxide.

Chemistry around us

In 1902 pure radium Ra was obtained by the French-Polish physicist Marie and Pierre Curie from the uranium mineral. They received 0.1 g of radium from 1 ton of ore. Curie and their colleagues found that radioactive radium destroys the tumor.



Chemfact

The atmosphere of Venus consists of carbon dioxide, nitrogen and other compounds are present in trace amount. Also contains sulfuric acid clouds, which make it impossible to observe the surface in visible light. There are acid rains in the upper layers of the Venus troposphere.

Terminology

- yield of reaction - реакция шығымы / выход реакции;
- tumor - ісік / опухоль;
- trace amount - аз мөлшерде / незначительные, следовые

количества.

QUESTIONS AND PROBLEMS

1. Identify and calculate the number particles in each of the following quantities.

- - 4.02 moles of silver
- - 0.3 mole of nitrogen dioxide
- - 2.46 moles of magnesium chloride

2. Calculate the number of moles of the substance that contains the following number of representative particles.

- - 5.9 • 1023 atoms of sodium
- - 1.32 • 1025 molecules of lithium hydroxide
- - 43.696 • 1020 formula units of hydrogen chloride

3. Determine the mass in grams of each of the following quantities.

- - 0.25 moles of phosphorus
- - 0.39 mole of carbon

4. Which quantity has the greatest mass?

- - 9.25 • 1023 atoms of nitrogen atom
- - 8.399 • 1023 atoms of calcium
- - 1.21 • 1026 atoms of aluminum

5. Calculate the number of moles in each of the following samples.

- - 8.39 g calcium oxide CaO
- - 400 g ammonium nitrate NH4NO3

6. Use this equation to solve the following mole-to-mole problems

$2H_2S + O_2 \rightarrow 2S + 2H_2O$

- \- If you want to make 23 moles of sulfur, how many moles of H_2S will you need?
- \- If you have 15 moles of oxygen, how many moles of water can you make?
- \- If you have 70 moles of H_2S, how many moles of oxygen will you need? How many moles of sulfur S will that make?

7. How many grams of sulfuric acid H_2SO_4 are required to make 710 grams of hydrogen chloride HCl?

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

8. How many moles of copper are reacted with with 3.5 moles of nitric acid HNO_3?

$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

9. How many tons of iron Fe can be made from 5 tonns of magnetite Fe_3O_4?

$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$

10. How many grams of oxygen O_2 are required to react with 0.26 mole of carbon dioxide CO_2?

$2CO + O_2 \rightarrow 2CO_2$

11. How many grams of oxygen O_2 can be produced from 150 grams of hydrogen peroxide H_2O_2?

$H_2O_2 \rightarrow H_2O + O_2$

12. How many grams of calcium carbonate $CaCO_3$ can be made from 540 grams of calcium hydroxide $Ca(OH)_2$?

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

13. The balanced equation given below

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

- - How many grams of calcium carbide CaC_2 can be reacted with 200 grams of water?
- - How many grams of water are required to react with 86 grams of calcium carbide?

14. How many grams of oxygen O_2 are required for the burning of 450 grams of butane C_4H_{10} according to the following balanced equation?

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

15. For the balanced equation in question 8, how many grams of carbon dioxide are made at the same time that 444 grams of water are produced?

16. For all these mole-to-gram problems, use the following balanced equation.

$2FeS_2 + 11O_2 \rightarrow Fe_2O_3 + 4SO_2$

- - How many grams of iron (III) oxide Fe_2O_3 can be produced from 80 moles of pyrite FeS_2?

- - If there are 7 moles of oxygen O_2, how many grams of pyrite FeS_2 are needed?
- - At the same time that 150 moles of sulfur dioxide SO_2 are produced, how many grams of iron (III) oxide Fe_2O_3 are also produced?

17. For all these gram-to-mole problems, use the following balanced equation.

$Al_2S_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2S$

- - How many moles of aluminum sulfide Al_2S_3 are needed to react with 60 grams of oxygen O_2?
- - In order to get 200 grams of aluminum hydroxide $Al(OH)_3$, how many moles of water are needed?
- - How many moles of hydrogen sulfide H_2S would be the result of reacting 90 grams of O_2?

18. Which one of the following is/are conserved in the following reaction?

$H_2 + 2K \rightarrow 2KH$

I. Number of atoms

II. Number of molecules

III. Total mass

19. When 44.1 g of lithium (Li) reacts with chlorine Cl_2 267.75 g of lithium chloride (LiCl) is formed. What is the mass of chlorine reacted?

20. The reaction 39.2 g of KOH with 44.1 g of HNO_3 produces

KNO_3 and 12.6 g of water. What is the mass of KNO_3 produced?

$KOH + HNO_3 \rightarrow KNO_3 + H_2O$

21. The reaction 18 g of ethane C_2H_6 with 67.2 g of oxygen O_2 produces 52.8 g of carbon dioxide CO_2 and water. What is the mass of water produced?

$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

22. The reaction 11.2 L of H_2 with 11.2 L of Cl_2 produces hydrogen chloride HCl. How many liter of HCl produced?

$H_2 + Cl_2 \rightarrow 2HCl$

23. The reaction 4.48 L of ammonia NH_3 with 5.6 L of oxygen O_2 produces nitrogen monooxide NO and 6.72 L of water vapor. How many liter of nitrogen monooxide NO produced?

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

24. For each of these problems find out which reactant is the limiting factor. Then calculate the number of grams of water made and the number of moles of excess. Use the following balanced equation for calculations.

$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$

- - For 50 moles of each reactant, which is the limiting factor, how many grams of water are produced, and how grams of excess remain?

- - Perform the same three calculations when there are 46 grams of each reactant.
- - Perform the same three calculations when there are 800 grams of benzene C_6H_6 and 600 grams of oxygen O_2.

25. Which reactant is the limiting reagent if there are 80 grams of fluorine and 60 grams of sulfur? How many grams of sulfur hexafluoride SF_6 can be produced?

$S + 3F_2 \rightarrow SF_6$

26. How many moles of oxygen are required to react with 5.6 moles of ethanol C_2H_5OH?

$C_2H_5OH + O_2 \rightarrow CO_2 + H_2O$

27. How many grams of NH_3 can be made from 5.6 grams of hydrogen and 5.6 grams of nitrogen?

$N_2 + 3H_2 \rightarrow 2NH_3$

28. 47.81 g of gas NX_3 occupies 63 L at STP conditions. What is the atomic mass of element X?

29. 40 g of unknown gas XO has volume 32 L at STP conditions. Calculate the atomic mass of element X.

30. 63.47 L of X_2H_6 gas at STP conditions has mass 85 g. What is the atomic mass of element X?

31. How many grams of hydrogen iodide HI can be form when 2.26 L of hydrogen gas completely reacts with iodine?

$H_2 + I_2 \rightarrow 2HI$

32. What volume of oxygen gas is needed for the complete combustion of 89 L of ethane C_2H_6 gas? Assume that pressure and temperature remain constant.

33. How many liters of chlorine gas Cl_2 are needed to react with 70 g of NaOH at STP?

$3Cl_2 + 6NaOH \rightarrow 5NaCl + NaClO_3 + 3H_2O$

34. How many liters of chlorine gas H_2 are needed to react with 64 g of carbon dioxide CO_2 at STP?

$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

35. How many liters of NO gas at STP can be formed when 3.2 g of copper metal reacts with an excess amount of diluted nitric acid HNO_3?

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

36. How many liters of laughing gas N_2O at STP can be formed when 8.9 g of magnesium reacts with an excess amount of diluted nitric acid HNO_3?

$4Mg + 10HNO_3 \rightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$

37. How many liters of nitrogen gas N_2 (at STP) can be formed when 80 g of tin Sn reacts with an excess amount of diluted nitric acid HNO_3?

$5Sn + 12HNO_3 \rightarrow 5Sn(NO_3)_2 + N_2 + 6H_2O$

38. What is the mass of marble $CaCO_3$ should be used to obtain 78 L of CO_2 gas according to the equation below?

$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

39. What is the mass of ammonium dichromate $(NH_4)_2Cr_2O_7$ should be used to obtain 45.3 L of water vapor according to the equation below?

$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$

40. Decomposition of $AgNO_3$ undergoes according to the chemical equation:

$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$

Calculate the volume of gases produced from the decomposition 870 g of $AgNO_3$?

41. Decomposition of $Fe(NO_3)_2 \cdot 6H_2O$ undergoes according to the chemical equation:

$4\{Fe(NO_3)_2 \cdot 6H_2O\} \rightarrow 2Fe_2O_3 + 8NO_2 + O_2 + 24H_2O$

Calculate the volume of NO_2 produced from the decomposition 1200 g of $Fe(NO_3)_2 \cdot 6H_2O$?

42. How many liter of hydrogen gas can be obtained from the reaction 21.6 g of aluminium and hydrochloric acid HCl?

43. How many liter of sulfur dioxide SO_2 gas can be obtained from the reaction 85.1 g of pyrite FeS_2 and oxygen?

$2FeS_2 + 11O_2 \rightarrow Fe_2O_3 + 4SO_2$

44. 3.2 grams of CaO is produced by the reaction between 4 grams Ca and 11.2 L of oxygen. Determine the percent yield of CaO.

45. If 95 g of $CaSO_3$ are decomposed and 39 g of CaO are obtained, what is the percent yield of CaO?

$CaSO_3 \rightarrow CaO + SO_2$

46. $2Fe + 3Cl_2 \rightarrow 2FeCl_3$

A student conducted the above chemical reaction in a lab as a part of his research assignment. He used 7.3 g of iron with excess amount of chlorine gas. What is the percent yield of $FeCl_3$, if the actual yield of $FeCl_3$ was 18.2g?

5
CHAPTER

INTRODUCTION TO THERMODYNAMICS

CHAPTER 5: INTRODUCTION TO THERMODYNAMICS

5.1 INTERNAL ENERGY AND ENTHALPY

Why do fats release more energy than carbohydrates?

You will:

- understand that changes in internal energy and enthalpy are thermal effects;
- understand that chemical reactions include the processes of breaking bonds and forming new chemical bonds.

Enthalpy change of reactions

Molecules store certain amount of energy. This energy is known as internal energy, which is shown by a symbol U. We cannot measure total internal energy directly, because it contains any form of energy which is stored in a system. We can only calculate the change of internal energy. The change of internal energy occurs by transfer of either heat (Q) or work (W), or both. So:

$$\Delta U = Uf - Ui = Q + W$$

However, in chemistry we are mainly interested in the heat exchanges of the processes, specifically the changes that occur at constant pressure (as most of the processes we observe happen at 1 atm). A state function which we are going to use to calculate heat transfers at constant pressure is called an enthalpy.

$$\mathbf{H = U + PV}$$

There is no exact amount of enthalpy, so we can calculate the change of enthalpy (ΔH) of the process. As we mentioned earlier, the heat transferred during a chemical reaction at constant pressure equals ΔH. So, at constant pressure:

$$\mathbf{\Delta H = Q}$$

The negative and positive signs of ΔH only represent the direction of heat changes. A negative sign "–" means loss of energy, while a positive sign "+" means the gain of energy for a reaction.

Enthalpy change of a reaction can be calculated as follows;

$$CH4(g) + 2O2(g) \rightarrow CO2(g) + 2H2O(g) + 890.5\ kJ \text{ and } \Delta H = -890.5\ kJ$$

(Here Σ means sum)

Burning of methane gas

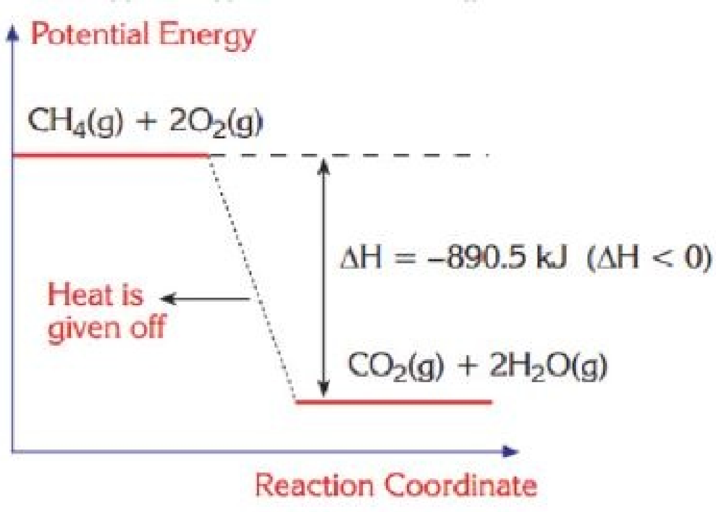
In exothermic reactions, ΣHproducts< ΣHreactants, so the ΔH has a negative sign (ΔH<0). For example

$$\mathbf{\Delta H = \Sigma H products - \Sigma H reactants}$$

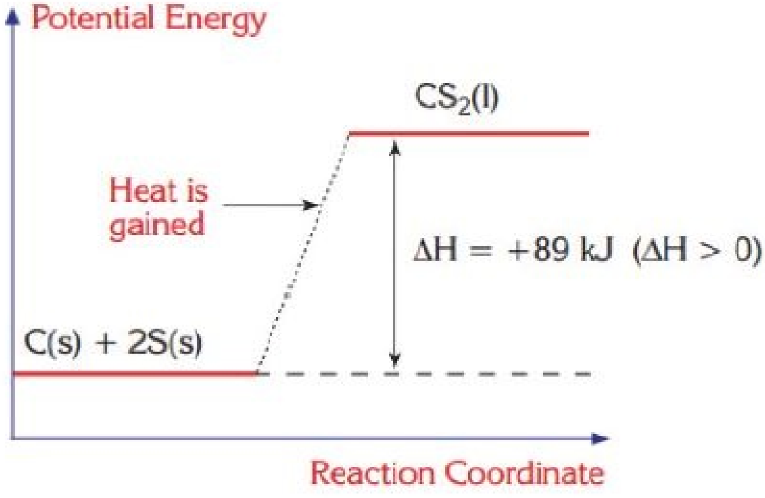
In endothermic reactions, ΣHproducts> ΣHreactants, Hence, the

ΔH has a positive sign (ΔH>0). For example

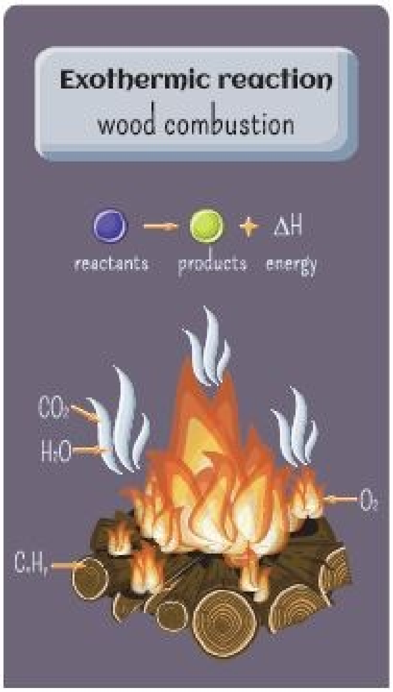
$$C(S) + 2S(s) + 89 \text{ kJ} \rightarrow CS2(l) \text{ and } \Delta H = +89 \text{ kJ}$$



An exothermic reaction



An endothermic reaction



Bond breakage and bond energy

Atoms are held together in molecules by chemical bonds. During the reaction, all bonds of the atoms must be broken. Therefore, energy is required to break these bonds. It must be taken in to pull the atoms apart. The energy that is consumed to break one mole of a covalent bond in a molecule in the gaseous state is known as Bond Energy. For example, 243 kJ of energy is required to break 1 mol Cl – Cl bond.

$$\text{Cl – Cl} + 243\ \text{kJ} \rightarrow \text{Cl}\bullet + \text{Cl}\bullet$$

Bond energies of some molecules are given in the table.

Table 8 *Bond Energies*

Bond	Bond Energy (kJ/mol)	Bond	Bond Energy (kJ/mol)
Br – Br	193	Cl – Cl	243
C – C	347	F – F	153
C = C	612	H – Br	368
C ≡ C	820	H – Cl	431
C – Br	276	H – F	565
C – Cl	326	H – H	435
C – F	485	N – H	389
C – H	414	N – N	159
C – O	335	N ≡ N	941
C = O	715	O – H	463

In a bond formation between two atoms, energy is released. The amount of this formation energy is exactly the same as the bond energy of the atoms. In a chemical reaction, bonds on the reactants' side are broken and new bonds are produced on the products' side. So, the heat of a reaction is the difference between the total amount of energy of bond breakages and bond formations.

$$\Delta H = \Sigma H\text{bond breakage} - \Sigma H\text{bond formation}$$

Some bonds are stronger than others, accordingly, they require more energy to break them, but when they form a new bond, they produce more energy.

Breaking a chemical bond is an endothermic process. Because it absorbs energy from the surroundings. Making a chemical bond is an exothermic process. It releases energy to the surroundings.

Chemistry around us

Where does the Earth take energy?

Despite the fact that the distance between the Sun and the Earth is 149 600 000 km, the Sun controls the climate on Earth. The Earth absorbs heat energy from the Sun using radiation.

Research time

Open in browser Endothermic reaction (Ba(OH)2+NH4SCN).

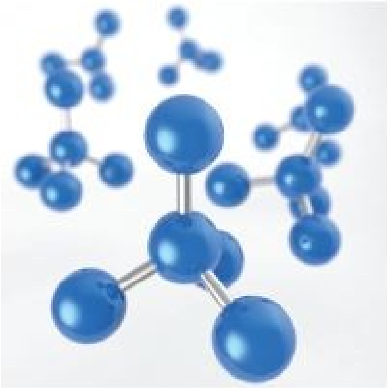
Why endothermic reactions occur if the enthalpy of the system increase, therefore system stability decreases?

Why is photosynthesis considered an endothermic reaction?

Why in an endothermic reaction does the temperature decrease?

Keep in mind

Breaking a chemical bond is an endothermic process. Because it absorbs energy from the surroundings. Making a chemical bond is an exothermic process. It releases energy to the surroundings.



Atoms are held together in molecules by chemical bonds

Example 1

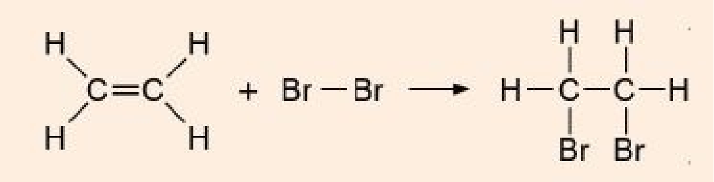
Find the ΔH of the reaction:

C2H4 + Br2 → C2H4Br2

by using bond energies.

Solution

Ethylene reacts with bromine to produce 1,2-dibromoethane.



According to the bond energies from the table.

C-H → 414 kJ/mol

C=C → 612 kJ/mol

Br-Br→ 193 kJ/mol

C-Br → 276 kJ/mol

C-C → 347 kJ/mol

ΔH = Σ Hbond breakage - Σ Hbond formation

Bond Breakage Bond Formation:

4(C – H) = 4 • 414 = 1656; 4(C – H) = 1656

1(C = C) = 612

2(C – Br) = 2 • 276 = 552

1(Br – Br) = 193

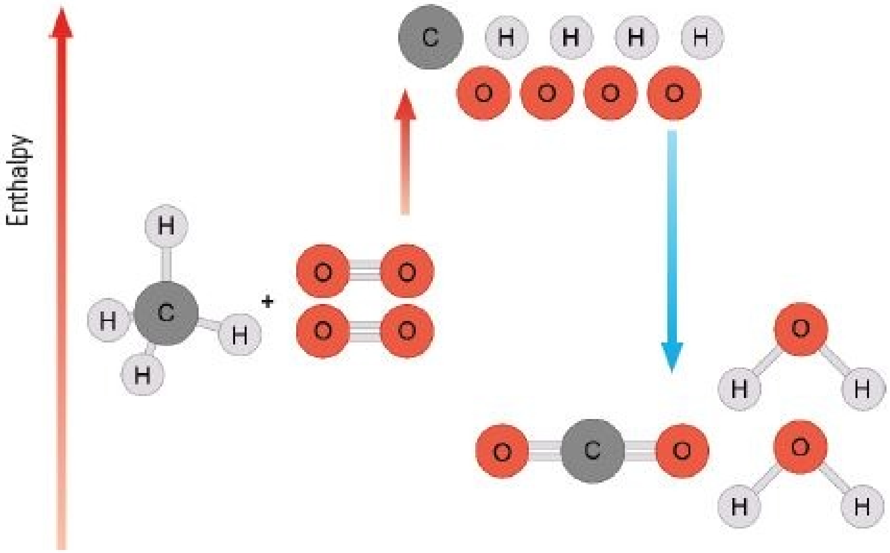
1(C – C) = 347

Finally:

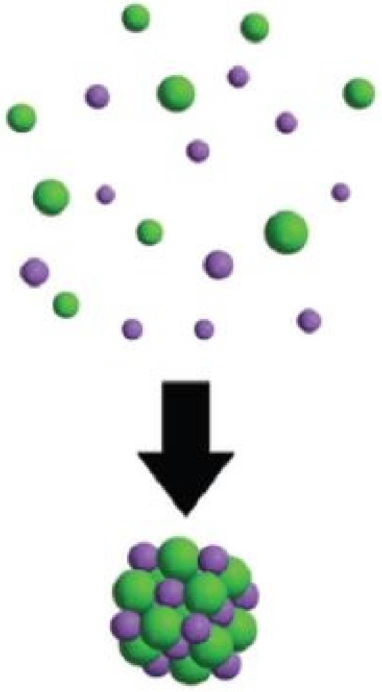
ΔH = (+1656 + 612 + 193) – (1656 + 552 + 347)

ΔH = +2461 – 2555 = – 94 kJ

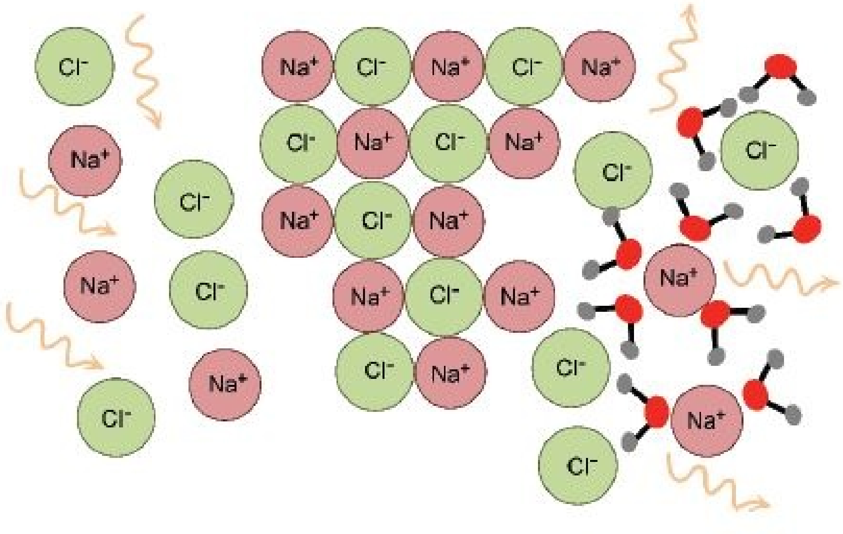
When ethylene reacts with bromine, the total energy released is bigger than the total energy absorbed. So, as a result, the reaction gives out energy - it is an exothermic reaction.



Enthalpy diagram of methane combustion



Recrystallization of sodium chloride



Dissociation of NaCl

Literacy

1. Calculate the heat of reaction, ΔH, for the reaction

CH4(g) + 4Cl2(g) → CCl4(g) + 4HCl(g)

by using the bond energies

2. 2CuS(s) + 3O2(g) → 2CuO(s) + 2SO2(g)

What is the value of ΔHo for the reaction given above?

3. O2(g) + 2H2O(l) + 4NO2(g) → 4HNO3(l)

What is the value of ΔHo for the reaction given above?

4. Find the ΔHo for the reaction:

C2H4 + H2 → C2H6

by using bond energies.

5. CH4 + 2Cl2 → CH2Cl2 + 2HCl

Find the ΔHo for the reaction by using bond energies.

Terminology

- internal energy - ішкі энергия / внутренняя энергия
- enthalpy - энтальпия / энтальпия
- bond breakage - байланысты үзу / разрыв связи
- require - қажет / требуется

5.2 SOLVING PROBLEMS: INTERNAL ENERGY AND ENTHALPY

Why do some materials (for example, metallic) conduct heat better than others?

You will:

- experimentally change the enthalpy of the reaction and calculate it on the basis of reference data.

Let’s solve some problems related to thermochemical reactions.

Calorimeter and thermometer.

Example 1

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.5$ kJ/mol

Answer the following questions for the reaction given above:

a. Is it exothermic or endothermic?

b. How many moles of CH_4 must be used to produce 356.2 kJ energy?

c. When 2.2 g of CO_2 is obtained, how much heat will be released?

Solution

a. $\Delta H < 0$. So, the reaction is exothermic.

b. According to the balanced equation, $\Delta H = -890.5$ kJ/mol means that if 1 mol of CH_4 reacts with a sufficient amount of oxygen gas, 890.5 kJ heat is produced.

Hence,

1 mol CH_4 produces ---- 890.5 kJ heat

x mol CH_4 produces ---- 356.2 kJ heat

$x = (1 \cdot 356.2) / 890.5 = 0.4$ mol CH_4

c. $Mr(CO_2) = 44$ g/mol

When 1 mol of CO_2 produced, 890.5 kJ heat is released.

In the formation of

44 g of CO_2 ----- 890.5 kJ heat is released

2.2 g of CO_2 ----- x kJ

$x = (2.2 \cdot 890.5) / 44 = 44.525$ kJ

Example 2

The reaction below, which is known as a thermite reaction, is highly exothermic.

$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$, $\Delta H = -850$ kJ

How much heat is emitted when 36 g of Al reacts with excess Fe_2O_3?

Solution

$Mr(Al) = 27$ g/mol

n(Al) = m / Mr = 36 / 27 = 1.33 mol

When

2 mol Al is consumed ---- 850 kJ heat released

1.33 mol is Al consumed ---- x kJ

x = (1.33 • 850) / 2 = 565.25 kJ

Specific heat capacity

Some substances get hot and cool down very easily, for example, metals like iron. However, other substances, like water, require a lot of thermal energy to raise the temperature.

Specific heat capacity (c) - is the amount required to raise the temperature of one mass unit of a substance by 1.0°C.

Heat change = mass(m) × specific heat capacity(c) × temperature change (ΔT)

$$Q = m \times c \times \Delta t$$

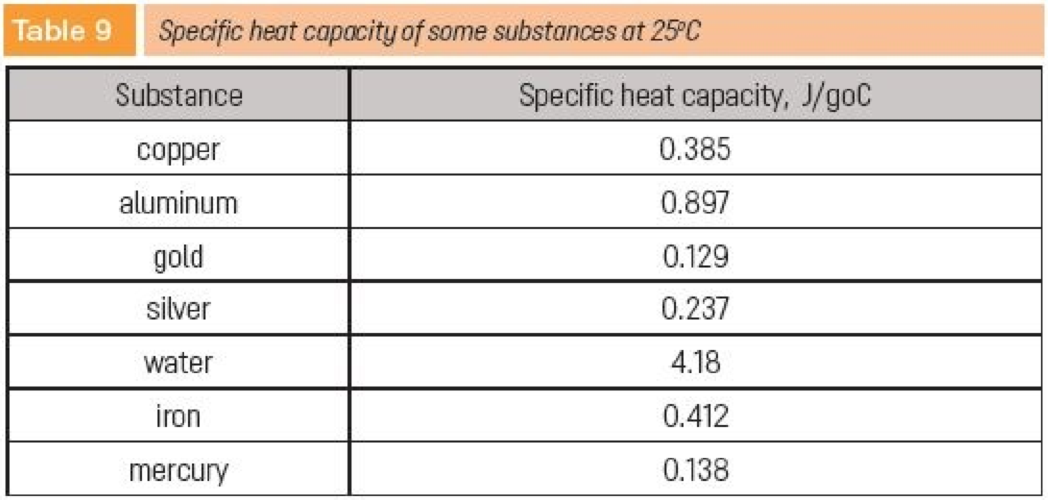


Table 9 *Specific heat capacity of some substances at 25°C*

Substance	Specific heat capacity, J/goC
copper	0.385
aluminum	0.897
gold	0.129
silver	0.237
water	4.18
iron	0.412
mercury	0.138

Example 3

How much heat is released during the process if 10 g of copper is cooled from 100oC to 40oC. (ccopper = 0.385 J/goC)

Solution

$\Delta H = m \times c \times \Delta t$

$\Delta H = -(10.0 \cdot 0.385 \cdot 60.0) = -231\ J$

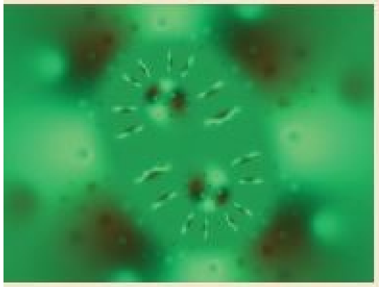
(the value is negative because Cu has lost heat)

Chemfact

Silver, gold, aluminum and copper are the best conductors of heat and electricity.

Chemistry around us

Silica aerogel is poor conductor of heat (thermal insulator). Aerogels are new synthetic materials that consist 99.98 % of air.



Practice work №1

Determination of the thermal effect of a neutralization reaction

Introduction:

The heat of neutralization is the amount of heat produced by neutralization (acid-base) reactions.

Neutralization only occurs between H^+ and OH^- ions. From the $\Delta H_{neutralization}$ value, when 1 mol H^+ from acid is neutralized with 1 mol OH^- from base, 56 kJ heat is released. Neutralization reactions are exothermic reactions. Change in heat is equal to the specific heat capacity of the substance times its total mass times the change in temperature. So,

$\Delta H = m \cdot c \cdot \Delta T$ where, c(water) = 4.184 J/g•K

$m = m(HCl) + m(NaOH)$

$\Delta T = T_f - T_i$

Materials:

0.1 M hydrochloric acid, 0.1 M sodium hydroxide, calorimeter (insulated container with a thermometer).

Procedure:

1. Pour 100 ml of hydrochloric acid into the calorimeter.

2. Note the temperature of your solution with the thermometer.

3. Pour 100 ml of sodium hydroxide into the calorimeter with the acid.

4. Check the temperature of the final solution.

5. Make the calculations and find the thermal effect of this neutralization reaction.

Safety: Wear gloves during the experiment.

Literacy

1. 1000 J of heat is added to some substances including gold, silver, iron, and water. Their masses are the same. Which of them will have the largest temperature increase?

2. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.5$ kJ/mol

Answer the following questions about the reaction given above:

a. Is it exothermic or endothermic?

b. How many moles of CH_4 must be used to produce 356.2 kJ energy?

c. When 2.2 g of CO_2 is obtained, how much heat will be released?

3. To produce 30.4 g of CS_2, how much heat must be gained by the reaction?

$C(s) + 2S(s) + 89\text{ kJ} \rightarrow CS_2(l)$

5.3 HESS'S LAW

Currently, around 1.3 billion people are living without access to modern energy. How to solve this problem?

You will:

- explain the physical meaning of Hess's law and use it to calculate the change in the enthalpy of chemical reactions;

Standard heat of formation

The heat change when 1 mol of a compound is produced from its elements under 1 atm pressure at 25°C in their most stable states is called standard heat of formation and is indicated by ΔH°f. The ΔH°f value of the free atoms (Na, K, Cu...) and free simple molecules (Cl2 , N2, O2, P4 etc.) is accepted as zero at standard conditions.

ΔH°f values for some molecules containing two or more different atoms are given in the table. Some other molecules are given in the Appendix A.

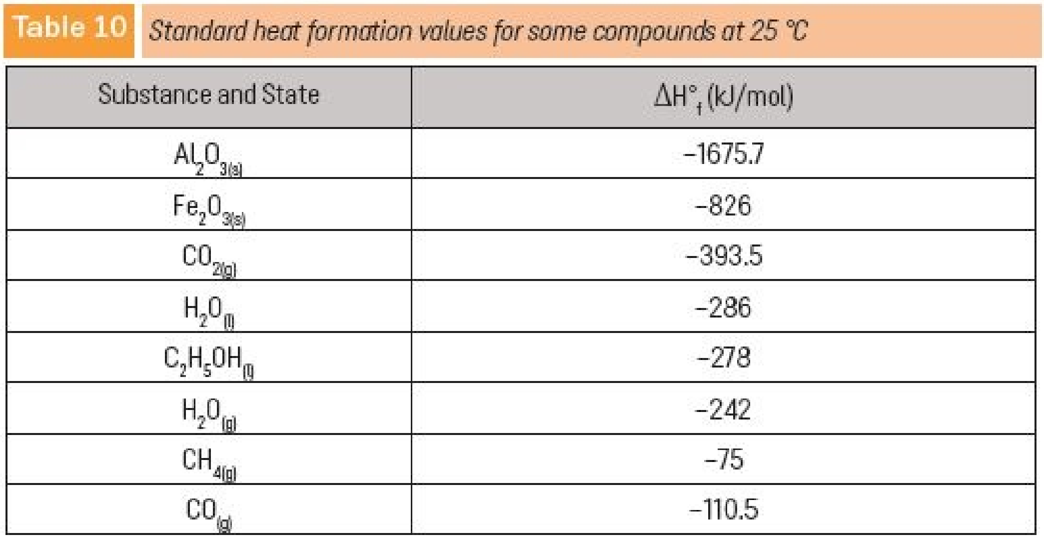


Table 10 *Standard heat formation values for some compounds at 25 °C*

Substance and State	$\Delta H°_f$ (kJ/mol)
$Al_2O_{3(s)}$	–1675.7
$Fe_2O_{3(s)}$	–826
$CO_{2(g)}$	–393.5
$H_2O_{(l)}$	–286
$C_2H_5OH_{(l)}$	–278
$H_2O_{(g)}$	–242
$CH_{4(g)}$	–75
$CO_{(g)}$	–110.5

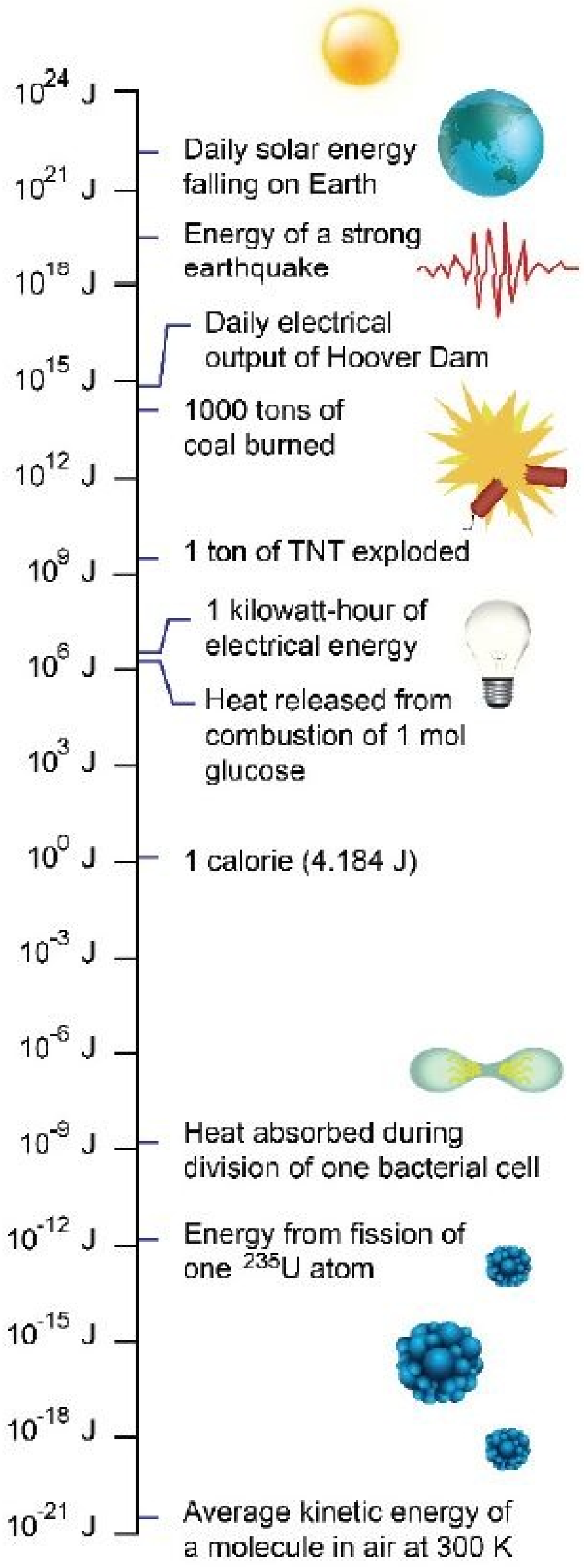
ΔH°f (CO_2) can be read from Table 1 as –393.5 kJ/mol, and expressed as;

$$C(graphite)(s) + O_2(g) \rightarrow CO_2(g)\ \Delta H°f = –393.5\ kJ/mol$$

$$2Al(s) + 3/2O_2(g) \rightarrow Al_2O_3(s)\ \Delta H°f = –1675.7\ kJ/mol$$

$$2Fe(s) + 3/2O_2(g) \rightarrow Fe_2O_3(s)\ \Delta H°f = –\ 826\ kJ/mol$$

The heat of a reaction, ΔH°, can be calculated by using ΔH°f values as follows.



Energy diagram

Hess’s Law

Hess’s law states that enthalpy change for any chemical reaction is constant, whether the reaction occurs in one or several steps. If a chemical reaction occurs in several steps, the enthalpy change of the total reaction will be the sum of enthalpy changes of the individual steps. For example, production of CO2 can be written in two steps:

$$\begin{array}{ll} \text{step 1: } C_{(graphite)(s)} + 1/2O_{2(g)} \rightarrow CO_{(g)} & \Delta H_1 = -110.5 \text{ kJ} \\ \text{step 2: } CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_{2(g)} & \Delta H_2 = -283.0 \text{ kJ} \\ & \Delta H = \Delta H_1 + \Delta H_2 \\ \text{Overall: } C_{(graphite)(s)} + O_{2(g)} \rightarrow CO_{2(g)} & \Delta H = (-110.5) + (-283.0) \\ & \Delta H = -393.5 \text{ kJ} \end{array}$$

Two Important Features of Hess’s Law

1. For the reverse reaction, ΔH for a reaction is equal in magnitude but opposite in sign to ΔH.

$$H2(g) + I2(g) \rightarrow 2HI(g), \quad \Delta H = +54 \text{ kJ}$$

For the reverse reaction,

$$2HI(g) \rightarrow H2(g) + I2(g), \quad \Delta H = -54 \text{ kJ}$$

2. ΔH is directly proportional to the amount of reactants or products. According to this statement, if the coefficients of a reaction equation are multiplied by a positive number, ΔH must also be multiplied by the same number.

$$H2(g) + I2(g) \rightarrow 2HI(g), \quad \Delta H1 = +54 \text{ kJ}$$

$$3H2(g) + 3I2(g) \rightarrow 6HI(g), \quad \Delta H2 = 3 \bullet \Delta H1 = 3 \bullet 54 = +162 \text{ kJ}$$

Example

I. $N_2(g) + O_2(g) \rightarrow 2NO(g)$ ΔH1 = +182 kJ

II. $NO_2(g) \rightarrow NO(g) + \frac{1}{2} O_2(g)$ ΔH2 = +58 kJ

By using the reactions above, find ΔH for the given reaction:

$1/2\ N_2(g) + O_2(g) \rightarrow NO_2(g)$

Solution

To obtain the final reaction, the first reaction must be divided by two and the second reaction must be reversed. Then, the two reactions must be summed up

I. $0.5\ N_2 + 0.5\ O_2 \rightarrow NO$ ΔH'1 = ΔH1/2 = +182 kJ / 2 = +91 kJ

II. $NO + 0.5\ O_2 \rightarrow NO_2$ ΔH'2 = -ΔH2 = - (+58) = -58 kJ

$0.5\ N_2 + O_2 \rightarrow NO_2$ ΔH = ΔH'1 + ΔH'2 = +91 + (-58) = +33 kJ

Literacy

1. I. $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l)$ ΔH1= -1532 kJ

II. $N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(l)$ ΔH2= -368 kJ

III. $H_2(g) + 0.5O_2(g) \rightarrow H_2O(l)$ ΔH1= -286 kJ

By using the reactions above, find the ΔH for the following reaction:

$2NH_3(g) + 3N_2O(g) \rightarrow 4N_2(g) + 3H_2O(l)$

2. I. $C(s) + 2H_2(g) + 0.5O_2(g) \rightarrow CH_3O(l)$ ΔH1= -239 kJ

II. $H_2(g) + 0.5O_2(g) \rightarrow H_2O(g)$ $\Delta H_1 = -242$ kJ

III. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_2 = -393.5$ kJ

By using the reactions above,

a) Find the molar heat of combustion of CH_3OH:

b) If 8 g of CH_3OH is burnt, how much heat will be released?

3. When 2.4 g of graphite are burnt completely 78.70 kJ heat is released; what is the molar heat of formation of CO_2?

4. $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

What is the value of $\Delta H°$ for the reaction given above?

5. $H_2(g) + 0.5O_2(g) \rightarrow H_2O(g)$ $\Delta H_1 = -242$ kJ

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_2 = -393.5$ kJ

$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$ $\Delta H_2 = -124.5$ kJ

By using the reactions above, find the ΔH(combustion) for C_4H_{10}.

Terminology

- standard heat of formation - стандартты түзілу жылуы / стандартная теплота образования
- Hess’s law - Гесс заңы / закон Гесса

5.4 ENTROPY

All systems tend to disorder rather than order. For example, in daily life after using long time our cell phones and electronic devices do not work well. Conversely, why old cell phones do not work well?

You will:

- explain entropy as a measure of disorder in the system and calculate it according to reference data;

The thermodynamic entropy S oft en referred to simply as entropy, is a physical quantity used to describe a thermodynamic system, one of the basic thermodynamic quantities. Entropy is a function of the state and is widely used in thermodynamics, including technical (analysis of the operation of thermal machines and refrigeration plants) and chemical (calculation of equilibrium chemical reactions).

Entropy is a measure of disorder. Visually, the more uniformly arranged things in a certain space, the greater the entropy. If sugar lies in a glass of tea in the form of a piece, the entropy of this state is small. If sugar is dissolved and distributed throughout the volume, then the entropy is great. Disorder can be measured, for example, by counting how many ways it is possible to decompose objects in a given space. If all socks are stacked extremely compactly with one stack on the shelf in the room, the number of layout options is small and reduces only to the number of permutations of socks in the stack. If the socks can be at any place in the room, then there is an unthinkable number of ways to decompose them, and these layouts do not repeat throughout our lives, like the shapes of snowflakes. The entropy of the state of "socks are scattered" is enormous.

In chemistry, the change in the enthalpy of the system can not be the only criterion for the spontaneous realization of a chemical reaction, since many endothermic processes occur spontaneously. An illustration of this is the dissolution of some salts (for example, NH4NO3) in water, accompanied by a noticeable cooling of the solution. It is necessary to take into account one more factor that determines the ability to spontaneously move from a more orderly to a less orderly (more chaotic) state.

The possibility of endothermic processes is due to a change in entropy, for in isolated systems the entropy of a spontaneous process increases $\Delta S > 0$ (the second law of thermodynamics). The entropy dimension of 1 mole of substance coincides with the dimension of the gas constant R and is equal to J • mol-1 • K-1. The change in entropy in irreversible and reversible processes is transferred by the relations $\Delta S > Q / T$ and $\Delta S = Q / T$. For example, the change in the entropy of melting is equal to the heat (enthalpy) of melting

$\Delta S_{melting} = \Delta H_{melting} / T_{melting}$.

For a chemical reaction, the change in entropy is analogous to the change in enthalpy.

$$\Delta S^0_{reaction} = \Delta S^0_{products} - \Delta S^0_{reactants}$$

The entropy of a substance or system of bodies at a certain temperature is an absolute value. The unit of entropy is J/(mol · K).

Probability of collision is high at high concentration

Disorder mess at home

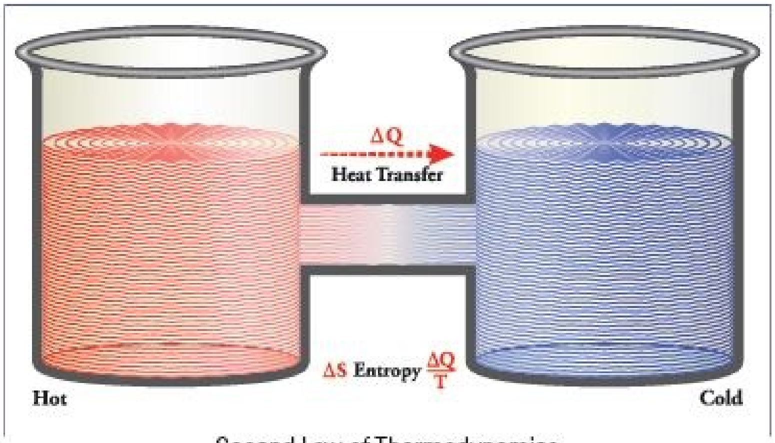
Traffic in India's largest city

Standard entropy

The values of entropy are usually referred to the standard state. Most oft en, the values of S are considered for P = 101.325 kPa (1 atm) and temperature T = 298.15 K (25 ° C). The entropy in this case is denoted by S°298 and is called the standard entropy at T = 298.15 K. It should be emphasized that the entropy of the substance S (S0) increases with increasing temperature.

Standard Entropy of formation

The standard entropy of the formation of Sof,298 is the change in entropy in the process of formation of the given substance (usually 1 mol), which is in standard state, from simple substances that are also in standard state.



Second Law of Thermodynamics

Example 1

Determine how the entropy changes during the following chemical process:

Na2O(s) + H2O(g) → 2NaOH(aq)

Solution

In this process, 1 mole of crystalline react with 1 mole of liquid substance to produce 2 moles of crystalline substance. Consequently, the system goes into a state with a smaller disorder, and the entropy decreases (ΔS<0).

Answer: decreases.

Example 2

Calculate the value of ΔSo298 for the following process. Use values of standard entropies of substances given in the table.

Na2O(s) + H2O(g) → 2NaOH(aq)

Solution

Using the reference data: So(NaOH(s)) = 64,16 J/(mol·K), So(Na2O(s)) = 75,5 J/(mol·K),

So(H2O(l)) = 70 J/(mol·K), let's calculate ΔSo298:

ΔSo298 = 2·So(NaOH(s))– [So(Na2O(s)) + So(H2O(l))] = 2 · 64,16 – (75,5 + 70) = – 17,18 J/K.

Example 3

Using thermodynamic reference data explain change in entropy and find its value.

Calculate the change in entropy in the reaction at 298.15 K:

4NH3(g) + 5O2(g) = 4NO(g) + 6H2O(g).

Substance	$NH_{3(g)}$	$O_{2(g)}$	$NO_{(g)}$	$H_2O_{(l)}$
S^0_{298}, J/(mol·K)	192,66	205,04	210,64	69,95

Solution

ΔSo298 =4So298(NO(g)) + 6So298(H2O(l)) - 4So298(NH3(g)) - 5So298(O2(g)) = 4×210,64 + 6×69,95 - 4×192,66 - 5×205,04 = - 533,58 J/K.

In this reaction, $S_{\text{chemical reaction}, 298} < 0$, which is confirmed by calculation.

Example 4

Using reference data on the values of So 298, determine the possibility of spontaneous reaction in an isolated system of the process at 298 K:

KClO3(s) = KCl(s) + 3/2O2(s).

Solution

ΔSo298 = 247.1 J / K.

ΔSo298 is greater than 0, therefore this process will proceed spontaneously in an isolated system at 298 K.

Example 5

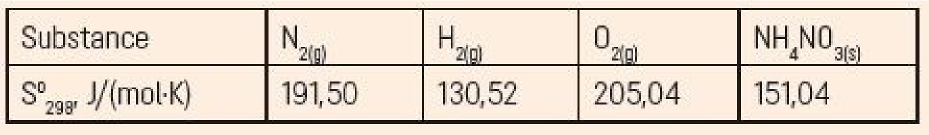
Using reference thermodynamic data, calculate the standard entropy of the formation of NH4NO3(s). Is the standard entropy of formation of NH4NO3(s) different from the standard entropy of this compound?

Solution

The standard entropy of NH4NO3 formation corresponds to a change in the entropy in the process:

N(g) + 2H2(g) + 3/2O2(g) = NH4NO3(s);

ΔSof,298(NH4NO3(s)) = ?



Substance	$N_{2(g)}$	$H_{2(g)}$	$O_{2(g)}$	$NH_4NO_{3(s)}$
S^o_{298}, J/(mol·K)	191,50	130,52	205,04	151,04

So298 =Sof,298(NH4NO3(s)) = So298(NH4NO3(s)) - So298(N2(s)) - 2So298(H2(s)) – 3/2So298(O2(s)) = 151,04 - 191,50 - 2×130,52 - 3/2×205,04 = - 609,06 J/(mol·K).

The standard entropy of the formation of NH4NO3(s), equal to -609.06 J / (mol · K),

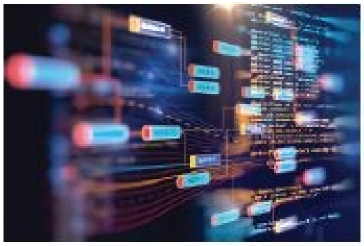
differs from the standard entropy of ammonium nitrate So298(NH4NO3(s)) = +151.04 J /(mol · K) and by the sign. It should be remembered that the standard entropy of So298 is always greater than zero, while the values of S0f,298 are, as a rule, alternating.

Chemfact

The concept of entropy was first introduced in 1865 by R. Clausius in thermodynamics to determine the measure of irreversible energy scattering. Entropy is used in various branches of science, including in information theory as a measure of the uncertainty of any experience, a test that can have different outcomes. These definitions of entropy have a deep inner connection.

Research time

Open in browser Entropy and Information. What is the relationship between entropy and information?



Keep in mind

When changing from an unequal state to an equilibrium state, entropy always increases.

Chemfact

Entropy increases when the material is heated. For example, the melting of ice is accompanied by an increase in the entropy of the ice-water system.

Literacy

1. Using reference data, determine the standard entropy of the formation of So298 NaHCO3(s).

2. Using reference data, calculate the change in entropy in the reaction at 298.15 K:

2NH4NO3(s) = 2N2(g) + 4H2O(g) + O2(g).

Explain the change in entropy and find its value.

3. Using reference data, calculate the entropy change in the process at 298 K:

$H2(g) + 1/2O2(g) = H2O(g)$.

4. Predict the sign of ΔSoreac and calculate its value for the combustion of 1 mol of methane at 25oC.

$CH4(g) + 2O2(g) = CO2(g) + 2H2O(g)$

5. Calculate the standard entropy change for the industrial synthesis of ammonia:

$3H2(g) + N2(g) = 2NH3(g)$

Terminology

- entropy - энтропия / энтропия
- disorder - ретсіздік / беспорядок
- accompanied - сонымен бірге жүретін / в сопровождении

5.5 GIBB'S ENERGY

In daily life, we observe the burning of wood or coal by leaving ash, but we do not see the opposite process of "unburning" of ash to form coal or wood. How to explain this observation?

You will:

- explain entropy as a measure of disorder in the system and calculate it according to reference data;

The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the system ($\Delta S_{system} > 0$). The Gibbs free energy (G), is a function that combines the reaction system's entropy and enthalpy:

$$\Delta G = H - T\Delta S$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Methane reacts with oxygen, to produce carbon dioxide and water. To know the reaction proceeds or not, it is necessary to determine the Gibbs energy of the reaction. Enthalpy and entropy determine Gibbs energy.

The spontaneous flow of the reaction is determined with two factors:

- enthalpy, associated with a decrease in the enthalpy of the system (ΔH),

- and entropy TΔS, caused by an increase in the disorder in the system due to the growth of its entropy. The difference between these thermodynamic factors is called the Gibbs free energy (G, kJ).

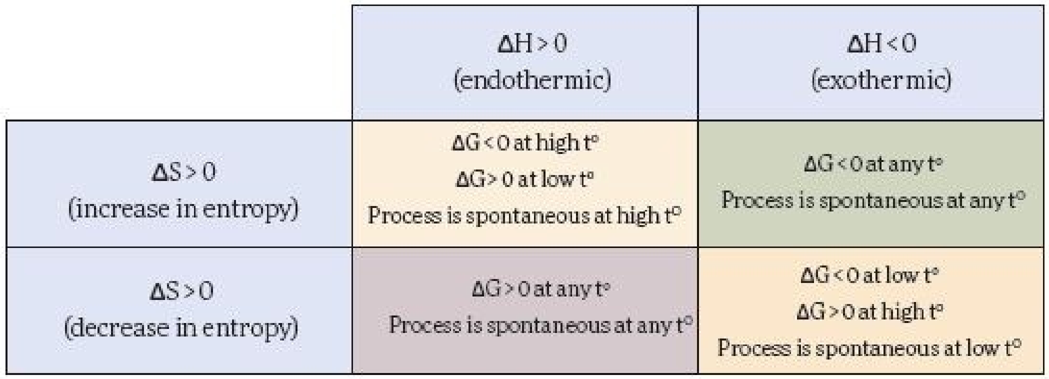
If $\Delta G < 0$, the reaction is thermodynamically resolved, and the system tends to reach the condition $\Delta G = 0$, at which the equilibrium state of the reversible process sets in; $\Delta G > 0$ indicates that the process is thermodynamically impossible.

In chemical reactions, the enthalpy factor and the degree of chaos (entropy factor, an energy that does not work) simultaneously change. If $\Delta H < 0$ and $\Delta S > 0$, then always $\Delta G < 0$ and the reaction is possible at any temperature.

If $\Delta H > 0$ and $\Delta S < 0$, then always $\Delta G > 0$, and the reaction with heat absorption and decreasing entropy is impossible under any conditions. In other cases ($\Delta H < 0$, $\Delta S < 0$ and $\Delta H > 0$, $\Delta S > 0$), the sign of ΔG depends on the ratio ΔH and TΔS.

A reaction is possible if it is accompanied by a decrease in the Gibbs energy; at room temperature, when the value of T is small, the value of TΔS is also small, and usually, the enthalpy change is higher than TΔS. Therefore, most of the reactions occurring at room temperature are exothermic. In high temperature, the greater TΔS, and even the endothermic reactions become realised.

$$\mathbf{\Delta Gorxn = \Sigma m\Delta Gof(products) - \Sigma n\Delta Gof(reactants)}$$



	ΔH > 0 (endothermic)	ΔH < 0 (exothermic)
ΔS > 0 (increase in entropy)	ΔG < 0 at high t° ΔG> 0 at low t° Process is spontaneous at high t°	ΔG < 0 at any t° Process is spontaneous at any t°
ΔS > 0 (decrease in entropy)	ΔG > 0 at any t° Process is spontaneous at any t°	ΔG < 0 at low t° ΔG > 0 at high t° Process is spontaneous at low t°

Summary of the four scenarios for Enthalpy and Entropy changes

Example 1

Calculating ΔGrxn from Enthalpy and Entropy values

Reaction of calcium carbonate with hydrochloric acid:

Fe2O3(s) + 2Al(s) → Al2O3(s) + 2Fe(s)

Use ΔHfo and So values to calculate ΔGorxn at 500°C for this reaction.

Solution

To solve for ΔGo, we need values from Appendix B. We use ΔHof values to calculate

ΔHorxn, use So values to calculate ΔSorxn, and then apply equation ΔG = H - TΔS.

Calculating ΔHorxn from ΔHfo values (Hess's law):

ΔHorxn = ΔHosys = ΣmΔHfo(products) - ΣnΔHfo(reactants) = [(1 mol Al2O3)•(ΔHfo of Al2O3) + (2 mol Fe) • (ΔHfo of Fe)] - [(1 mol Fe2O3) • (ΔHfo of Fe2O3) + (2 mol Al) • (ΔHfo of Al)] = [(1 mol) • (-1676 kJ/mol) + (2 mol) • (0 kJ/mol)] - [(1 mol) • (-825.5

kJ/mol) + (2 mol)• (0 kJ/mol)] = - 850.5 kJ

Calculating ΔSorxn from So values:

ΔSorxn = ΔSosys = ΣmSo(products) - ΣnSo(reactants) =

= [(1 mol Al2O3) • (ΔSo of Al2O3) + (2 mol Fe) • (ΔSo of Fe)] -

- [(1 mol Fe2O3) • (ΔSo of Fe2O3) + (2 mol Al) • (ΔSo of Al)] =

= [(1 mol) • (50.94 J/mol×K) + (2 mol) • (27.3 J/mol×K)] - [(1 mol) • (87.4 J/mol×K) + (2 mol) • (28.3 J/mol×K)] = -38.46 J/K

Calculating ΔGorxn at 773 K (500°C+273):

ΔGorxn = ΔHorxn - TΔSorxn = -850.5 kJ - [(500+273 K) • (-38.46 J/K)] = -820.77 kJ

All values are close to the calculated ones. Another way to calculate ΔGo for this reac tion is presented in Example 2

1. For a spontaneous reaction under any conditions, the free energy change, ΔG, is negative. Under standard-state conditions, a spontaneous reaction has a negative stan dard free energy change; that is, ΔGo < 0.

2. This reaction is spontaneous, and rate is high in the solid. Because hydrochloric acid is strong acid.

Example 2

Calculating ΔGorxn from ΔGof Values

Use ΔGof values to calculate ΔGorxn for the reaction in Example 1.

Fe2O3(s) + 2Al(s) → Al2O3(s) + 2Fe(s)

Solution

We apply equation ΔGorxn = ΔGosys = ΣmΔGof(products) - ΣnΔGof(reactants) to calculate ΔGorxn.

ΔGorxn = ΔGosys = ΣmΔGof(products) - ΣnΔGof(reactants) = [(1 mol Al2O3) • (ΔGof of Al2O3) + (2 mol Fe) • (ΔGof of Fe)] - [(1 mol Fe2O3) • (ΔGof of Fe2O3) + (2 mol Al) • (ΔGof of Al)] = [(1 mol) • (-1582 kJ/mol) + (2 mol) • (0)] - [(1 mol) • (-743.6) + (2 mol) • (0)] = - 838.4 kJ (at 25°C)

The slight discrepancy between this answer and that obtained in Example 1 is within experimental error. As you can see, when Gof values are available for a reaction taking place at 25°C, this method is simpler than that in Example 1.

Chemfact

In the human body, a lot of reactions of catabolism have a +G value and these reactions needs to get energy from other "coupled" reactions that have a negative value, so the total value is still negative. Many of them use hydrolysis of ATP to provide that energy, as its hydrolysis is about -30 kJ/mol in physiological conditions.

Literacy

1. Determine the standard free energy change at 298 K for the reaction

2N2(g) + O2(g) → 2NO(g).

2. Determine the standard free energy change at 298 K for the reaction

3H2(g) + N2(g) → 2NH3(g).

3. Use ∆Gof values to calculate the free energy change at 25°C for each of the following reactions:

- - BaCO3(s) → BaO(s) + CO2(g)
- - C2H5OH(l) + O2(g) → CO2(g) + H2O(l)

Terminology

- spontaneous - өздігінен / самопроизвольный;
- Gibbs free energy - Гиббстің еркін энергиясы / свободная энергия Гиббса.

QUESTIONS AND PROBLEMS

1. Explain the terms exothermic and endothermic.

2. Classify the following processes as exothermic or endothermic.

- \- When $NaNO_3(s)$ dissolves, the solution becomes cold.
- \- The burning of paper
- \- When concentrated H_2SO_4 is added to water, the solution gets warmer.
- \- Photosynthesis

3. Identify each of the following reactions as exothermic or endothermic:

- \- $Zn(s) + 2HCl(g) \rightarrow ZnCl_2(s) + H_2(g) + 230.5\ kJ$
- \- $4HBr(g) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)\ \Delta H = -426.4\ kJ$
- \- $N_2(g) + O_2(g) \rightarrow 2NO(g)\ \Delta H = +182.6\ kJ$
- \- $H_2O(g) + 241.8\ kJ \rightarrow H_2(g) + 1/2O_2(g)$

4. ΔH can be negative or positive; can the energy be negative? Explain

5. Write ΔH values for the given reactions:

- \- $CaCO_3(s) + 180\ kJ \rightarrow CaO(s) + CO_2(g)$
- \- $C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) + 1561\ kJ$
- \- $P_4(s) + 52.3\ kJ \rightarrow P_4(g)$

6. Which type of reaction absorbs energy from the surroundings?

7. Decomposition of hydrogen peroxide leads to production of water and oxygen.

$H_2O_2(g) \rightarrow H_2O(g) + O_2(g)$

Calculate the heat change of the reaction. Determine whether the reaction is endothermic or endothermic. Use following bond energies:

H-H = 436 kJ/mol;

O-H = 464 kJ/mol;

O-O = 144 kJ/mol;

O=O = 498 kJ/mol.

Is making a bond and exothermic or endothermic process?

Hess's law

1. From the following data at 25°C,

$\mathrm{H2(g) + Cl2(g) \rightarrow 2HCl(g)}\ \Delta H = -185\ \mathrm{kJ}$,

$\mathrm{2H2(g) + O2(g) \rightarrow 2H2O(g)}\ \Delta H = -483.7\ \mathrm{kJ}$

calculate ΔH at 25°C for the reaction below.

$\mathrm{4HCl(g) + O2(g) \rightarrow 2Cl2(g) + 2H2O(g)}$

2. Calculate ΔHo at 25°C for the reactions below

$\mathrm{BaCO3(s) \rightarrow BaO(s) + CO2(g)}$

$\mathrm{B2H6(g) + 3O2(g) \rightarrow B2O3(s) + 3H2O(g)}$

3. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are –890.3 kJ/mol, –393.5 kJ/mol, and –285.8 kJ/mol respectively. Find enthalpy of formation of CH4(g).

4. Enthalpies of formation of CO(g), CO2(g), N2O(g) and N2O4(g) are –110, – 393, 81 and 9.7 kJ/mol respectively. Find the value of ΔrH for the reaction:

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

5. Use Hess's law to determine the standard enthalpy of combustion of methane, $CH_4(g)$, given the following data:

$\Delta H^o_f(CO_2(g))=-393.5$ kJ/mol

$\Delta H^o_f(H_2O(l))=-285.83$ kJ/mol

$\Delta H^o_f(CH_4(g))=-74.81$ kJ/mol

6. Determine the standard heat of combustion of the sugar, sucrose $C_{12}H_{22}O_{11}$, to form $CO_2(g)$ and $H_2O(l)$, given that

$\Delta H^o_f(CO_2(g)) = -393.5$ kJ/mol

$\Delta H^o_f(H_2O(l)) = -285.83$ kJ/mol

$\Delta H^o_f(C_{12}H_{22}O_{11}(s)) = -74.81$ kJ/mol

7. Given that $\Delta H^o_f(FeCl_2(s)) = -341.8$ kJ/mol and $\Delta H^o_f(FeCl_3(s)) = -399.49$ kJ/mol, what is ΔH^o react (in kJ/mol) for the reaction:

$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$?

Enthalpy

1. The last step in the production of H_2SO_4 in industry is

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ $\Delta H = -266$ kJ

Calculate the amount of heat released when 1 kg of H_2SO_4 is produced?

2. How much heat is evolved in the formation of 86 g of $Fe_2O_3(s)$ at 25°C and 1 atm pressure by the following reaction?

$4Fe(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$

3. The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, CO2(g) and H2O are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, ΔfH0 of benzene. Standard enthalpies of formation of CO2(g) and 2H2O(l) are –393.5 kJ/mol and – 285.83 kJ/mol respectively.

4. Enthalpy of combustion of carbon to CO2 is –393.5 kJ/mol. Calculate the heat released upon formation of 35.2 g of CO2 from carbon and dioxygen gas.

Entropy

1. Determine ΔS for the following reactions

- - SO3(g) + H2O(l) → H2SO4(l)
- - S8(s) + O2(g) → SO2(g)
- - 2NaHCO3(s) → Na2CO3(s) + H2O(g) + CO2(g)
- - 2Al2O3(s) → 4Al(s) + 3O2(g)

2. Given the following data at 298 K, calculate

ΔS for the given reaction.

2AgNO3(s) → 2Ag(s) + 2NO2(g) + O2(g)

3. What is the change in standard entropy for the following reaction?

H2(g) + Cl2(g) → 2HCl(g)

4. Calculate the standard entropy change for the dimerization of NO2:

2NO2 ↔ N2O4

Gibbs energy

1. O3(g) + NO(g) → NO2(g) + O2(g)

From the following data, calculate the ΔGo in kJ for the reaction at 25oC and determine whether the reaction is spontaneous.

ΔHo = -199 kJ ΔSo = -4.1 J/K

2. For the reaction

H2(g) + S(s) → H2S(g),

ΔHo = -20.2 kJ ΔSo = 43.1 J/K. When will the reaction be spontaneous?

3. Calculate the ΔGo at 298 K for the following reaction.

Fe2O3(s) + 3C(s) → 2Fe(s) + 3CO(g)

4. Estimate the temperature at which ΔG = 0 for the following reaction.

NH3(g) + HCl(g) → NH4Cl(s)

ΔHo = 176 kJ, ΔSo = 284.5 J/K

5. Using the equation ΔG = ΔH - TΔS calculate the change in free energy for the following reaction

Fe2O3(s) + 3H2(g) → 2Fe(s) + 3H2O(g)

and determine if it will take place at

a) 30°C

b) 150°C

6
CHAPTER

KINETICS

CHAPTER 6: KINETICS

6.1 RATES OF REACTION

Why do small changes in temperature often have such large effects on the cooking rate of food?

You will:

- know expression of rate of reaction;
- calculate average and instantaneous rate of reaction.

The laws of thermodynamics make it possible to determine the direction and limit of the possible chemical process under the given conditions, as well as its energy effect. However, thermodynamics can not explain how this process is carried out and at what speed it takes place. The mechanism and rate of reaction - are the subject of chemical kinetics.

Introduction to kinetics

The word “kinetics” - derived from the Greek language “kinesis” which means - motion. And when we want to know how quickly something happens, the factor that we usually measure is time. You already have some general knowledge about rate of reaction from previous 9th grade. Let us give more strict definition: the rate of a reaction is the number of elementary chemical reactions occurring per unit time per unit volume (for homogeneous reactions) or per unit surface (for heterogeneous reactions). Usually in chemistry the dependence of the concentration of reactants on time is considered. It is obvious that concentrations of reactants always decrease ($\Delta C_{reactant} < 0$), and concentrations of products increase ($\Delta C_{product} > 0$). So mathematical expression of average rate of reaction is:

$$r = |\Delta C / \Delta t|$$

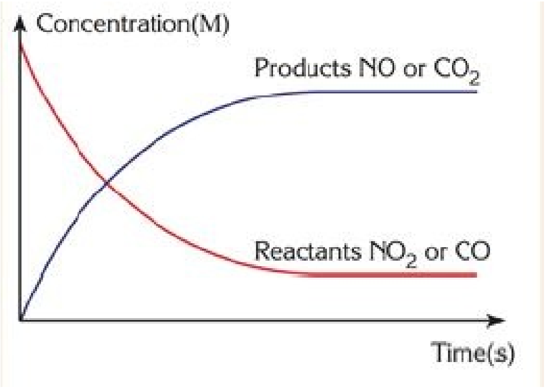
Let us consider a specific example.

Example 1

In the reaction,

$NO2(g) + CO(g) \rightarrow NO(g) + CO2(g)$

The graph of the process is represented as follows.



Solution

The rate of the reaction in terms of change in concentrations of reactants and products can be written as:

$r(NO2) = - (\Delta[NO2(g))])/\Delta t;$

$r(CO) = - (\Delta[CO(g))])/\Delta t;$

r(NO) = + (Δ[NO(g))])/Δt;

r(CO2) = + (Δ[CO2(g))])/Δt.

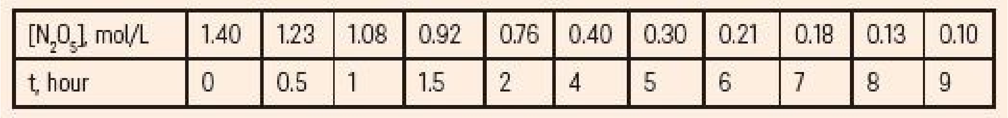
r(NO2) = r(CO) = r(NO) = r(CO2).

Calculation of rate of reaction by given graph

In natural sciences most of the equations are proved experimentally. And the aims of chemical kinetics are: 1) calculation of reaction rates and determination of kinetic curves that is the dependence of the concentrations of reactants on time (direct problem); 2) determination of the mechanisms of reactions by kinetic curves (inverse problem).

Example 2

The decomposition reaction of gaseous N2O5 with initial concentration of 1.4 mol/L at 30^{O}C takes place. NO2 and O2 are the product of the reaction. Write the reaction. Calculate the average rate of reaction in 30-90 minutes by given data:



[N_2O_5], mol/L	1.40	1.23	1.08	0.92	0.76	0.40	0.30	0.21	0.18	0.13	0.10
t, hour	0	0.5	1	1.5	2	4	5	6	7	8	9

Solution

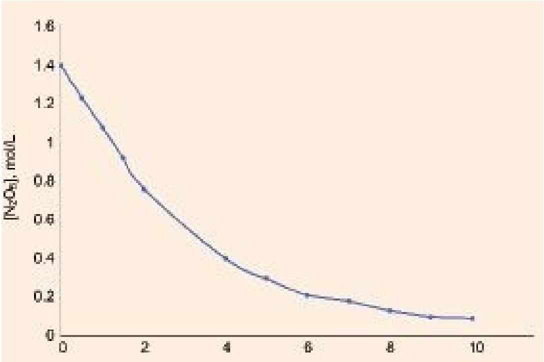
Reaction:

N2O5(g) → 2NO2(g) + O2(g).

r(30-90) = - Δ[N2O5] / Δt = - ([N2O5]90 - [N2O5]30) / (90 - 30) = - (0.92 - 1.23) / 60 = 0.0052 mol/(L•min) or 0.0052 M/min

Example 3

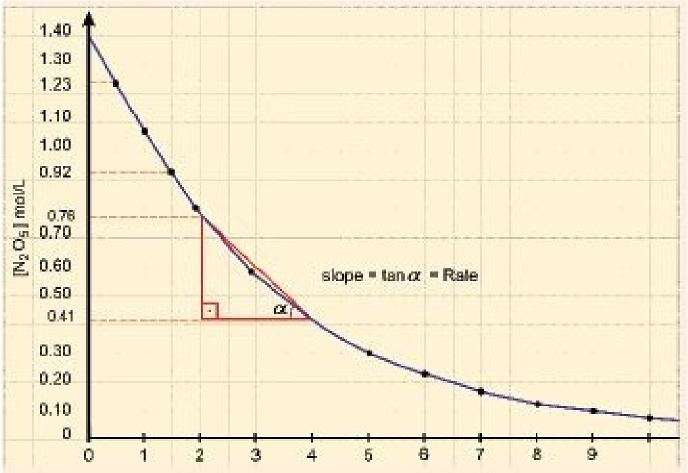
The product of the decomposition reaction of gaseous N2O5 at 30oC are NO2 and O2. Write the reaction. Calculate the instantaneous rate of reaction after 3 hour by illustrated graph:



Solution

The instantaneous rate at a point is found by calculating the slope of the line tangent to the curve at that point

Slope = tan(α) = r

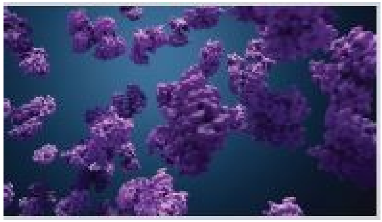


Instantaneous rate of reaction after 3 hours:

tan(α) = r = (0.76 - 0.41) / (240 - 120) = 0.0029 M/min.

Chemfact

Enzymes are incredibly efficient catalysts. Enzymes increase rates by 108 to 1020 times! For example, lysozyme, an enzyme found in tears, hydrolyzes bacterial cell walls, thus protecting the eyes from microbes, and chymotrypsin, an enzyme found in the small intestine, hydrolyzes proteins into smaller molecules during digestion.



Keep in mind

Concentrations of compounds C(X) in equations simplified and taken as [X]

Literacy

1. Find the rate relationship of reactants and products for the given reaction.

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$.

2. The reaction of hydrogen and chlorine to make hydrogen chloride at a particular temperature,

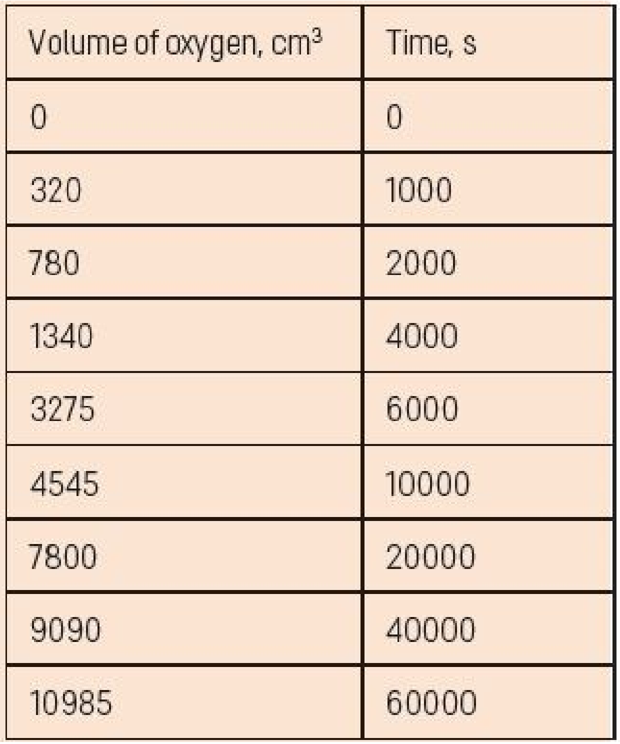
H2 + Cl2 → 2HCl

was studied at various times by stopping the reaction. At 90 s after the start of the reaction, the chlorine concentration had fallen from 0.01 mol/L to 0.0025 mol/L. What is the average rate of reaction during this period?

3. The rate at which a solution of hydrogen peroxide decomposes at 39oC,

2H2O2(l) → 2H2O(l) + O2(g)

was studied by monitoring the volume of oxygen gas produced with time:



Volume of oxygen, cm^3	Time, s
0	0
320	1000
780	2000
1340	4000
3275	6000
4545	10000
7800	20000
9090	40000
10985	60000

- - Plot the volume of oxygen against time.
- - Estimate the rate at which oxygen is produced at 20000 s.

Terminology

- average rate reaction - реакцияның орташа жылдамдығы / средняя скорость реакции;
- instantaneous rate of reaction - реакцияның лездік жылдамдығы / мгновенная скорость реакции;
- expression - өрнек / выражение;
- derived - алынған / полученный;
- is considered - қарастырылады / рассматривается;

6.2 EFFECT OF CONCENTRATION (FOR GASES, PRESSURE) ON THE RATE OF REACTIONS. RATE EXPRESSION

Why does food cooks faster in a pressure cooker than in boiling water?

You will:

- explain the application of rate expression;
- solve problems about rate expression;
- explain the effect of pressure on the rate of chemical reactions.

Concentration (pressure) effect

From the previous section you learned that the rate of reaction is determined by the change in concentration of the reacting substance per unit time. In practice, rate reaction can be determined by measuring concentrations of reactants at diff erent times. Rate of reaction depends on the concentrations of the reacting components.

As you remember increasing the concentration of reactants in terms of collision theory increases the rate of reaction.

For reactions involving gases, increasing pressure increases the rate of reaction. It happens because the higher pressure compresses the gas, effectively increasing its concentration. That's why the frequency of collision increases.

Probability of collision is low at low concentration

Probability of collision is high at high concentration

Rate expression

For the chemical reaction:

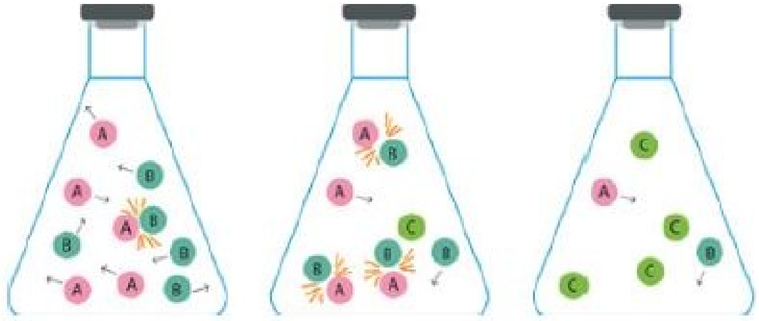
$$aA + bB \rightarrow cC$$

The reaction occurs as a result of the collision of particles A and B. The number of collisions is directly proportional to both the concentration of A and concentration B. So, rate of reaction can be expressed by given formula:

$$\mathbf{r = k \cdot [A]a \cdot [B]b \ ,}$$

[A] and [B] concentrations of reactants; a and b are stoichiometric coefficients of A and B respectively. k - reaction constant, which does not depend on concentration of reactants.

This equation represents mathematical expression one of the main laws of chemical kinetics called Rate expression. This law was discovered by Norwegian scientists Cato M. Guldberg and Peter Waage between 1864 and 1879.



The reaction between A + B substances and formation of substance C

Solid and liquid species are not included in the rate expression, since the concentration of solids and liquids is a constant. Gaseous substances and aqueous ions are indicated in the rate expression.

Example

Write rate expression for following reaction at 100oC:

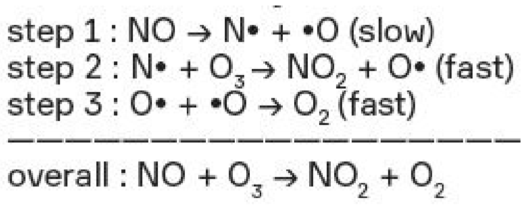
$2SO2(g) + O2(g) \rightarrow 2SO3(g)$.

Answer:

$r = k \bullet [SO2(g)]2 \bullet [O2(g)]$

Reaction mechanism

If the number of reactants in a reaction is small, the probability of this reaction to occur in a single step is very high. However, many reactions do not occur in a single step, but take place in a series of steps. Each step of a mechanism is called an elementary reaction, and a series of these reactions is called a reaction mechanism. The reaction between NO and O3 occurs in three steps.



step 1 : $NO \rightarrow N\bullet + \bullet O$ (slow)
step 2 : $N\bullet + O_3 \rightarrow NO_2 + O\bullet$ (fast)
step 3 : $O\bullet + \bullet O \rightarrow O_2$ (fast)

overall : $NO + O_3 \rightarrow NO_2 + O_2$

For any reaction mechanism, combining the steps must give the overall reaction. A reaction intermediate is a chemical species that is formed and consumed in a reaction, but does not appear in the overall balanced chemical equation. In the reaction above, O. and N. are the reaction intermediates.

The slowest step in a mechanism is the rate-determining step. That is, the rate of the overall reaction can be taken as the rate of the slowest step. Thus, the rate expression for the given reaction is:

$$\mathbf{Rate = k \bullet [NO]}$$

Keep in mind

The rate of reaction is directly proportional to the product of the concentrations of the reacting substances to the power of their stoichiometric coefficients.

Chemistry around us

Chemical kinetics has much application. Some of them are used as a manufacturer of medicine, radiometric dating in radiochemistry, used as a synthesis of organic and inorganic compounds.

Keep in mind

Radicals X• are highly reactive intermediate particles.

Keep in mind

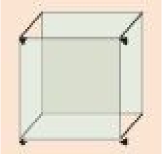
The slowest step of a mechanism determines its speed.

Literacy

1. Write rate expression for following reactions:

- $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$;
- $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$;
- $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$.

2. A cube of marble 2cm × 2cm × 2cm is cut into 4 smaller pieces along the dotted lines as shown:



- - What is the increase in surface area after cutting?
- - Explain why marble powder reacts more rapidly with sulfuric acid than marble blocks.

3. Find the rate relationship of reactants and products for the given reaction.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

4. 0.02 mol of SO_3 gas is produced in 1 L container within 5 minutes according to the reaction below. Find the rate of consumption of SO_2 and O_2 gases in M/s.

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

5. How does change rate of nitrogen dioxide production: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ if pressure in the system increases 3 times and temperature remains unchanged.

Research time

Open in browser Phet Reactions and Rates.

Sketch how the number of reactants and products will change as a reaction proceeds.

Terminology

- rate expression - жылдамдық өрнегі / выражение скорости;
- intermediates - аралық / промежуточный;

6.3 EFFECT OF TEMPERATURE: VAN’T-HOFF RULE AND ARRHENIUS EQUATIONS

When you get out of a swimming pool and stand wet in a breeze, you feel colder than after you dry off. Why?

You will:

- study effect of temperature and pressure experimentally;
- solve problems about Van't-Hoff rule;
- explain the physical meaning of the concept of "activation energy".

From qualitative considerations it is clear that the reaction rate should increase with increasing temperature, since this increases the energy of the colliding particles and increases the probability of the sufficient collision which causes chemical transformation. To describe the temperature effects in chemical kinetics, two main expressions are used: Van't Hoff rule and the Arrhenius equation.

We can simply define Van’t-Hoff rule as: the speed of most chemical reactions increase by 2-4 times when heated at each 10oC. Mathematically, this means that the reaction rate depends on the temperature in a power-law manner:

$$\frac{r(T_1)}{r(T_2)} = \gamma^{\frac{T_2-T_1}{10}}$$

where γ- temperature coefficient of rate of reaction (γ = 2 - 4).

The Van't Hoff rule is inaccurate and uses only in a very limited temperature range.

More accurate is the Arrhenius equation, which describes the temperature dependence of the rate constant:

$$k(T) = A \bullet \exp(-\frac{E_A}{RT})$$

where T - is temperature (K); R - is the universal gas constant (8.314 L•mol-1•K-1);

A - is a pre-exponential factor that does not depend on temperature, but is determined only by the type of reaction;

EA - is the activation energy, which can be characterized as a certain threshold energy: if the energy of the colliding particles is less than EA, then the collision will not occur if the energy exceeds EA, the reaction will occur. The activation energy does not depend on temperature.

- At low temperatures, chemical reactions almost do not occur: k(T) → 0.
- At very high temperatures the rate constant tends to the limiting value: k(T) → A. It means that all molecules are chemically active and each collision causes a reaction.

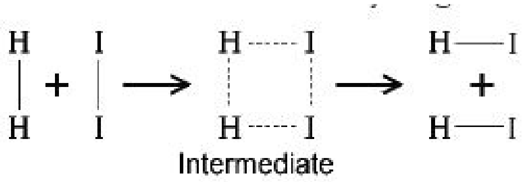
The activation energy can be determined by measuring the rate constant at two temperatures. From Arrhenius equation it follows that:

$$E_A = \frac{R \bullet T_1 \bullet T_2}{T_2 - T_1} \ln(\frac{k_2}{k_1})$$

It can be understood clearly using the following simple reaction.

$$H2(g) + I2(g) \rightarrow 2HI(g)$$

According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.



Formation of HI through the intermediate

The energy required to form this intermediate, called activated complex (C), is known as activation energy (E_A).

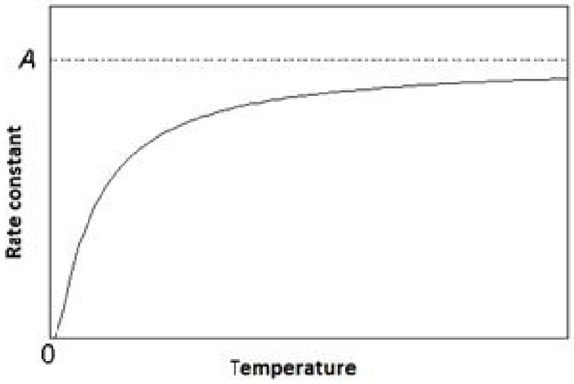


Diagram showing plot of rate constant of reaction and temperature

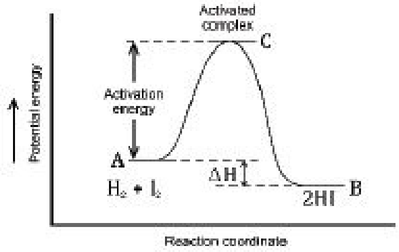
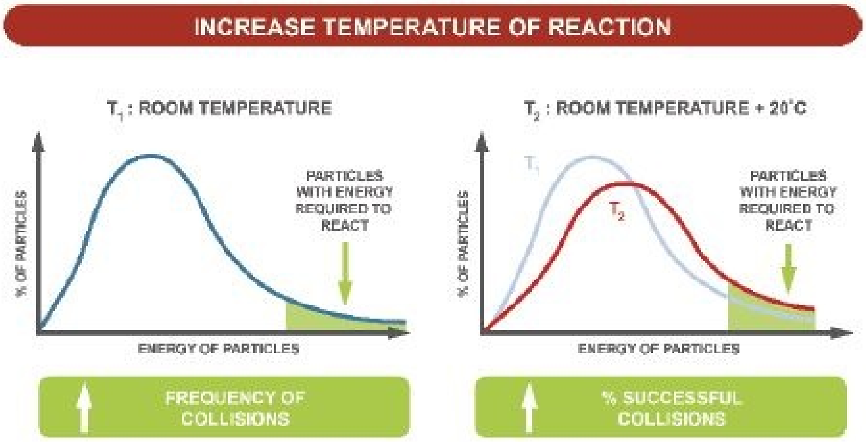


Diagram showing plot of potential energy vs reaction coordinate



Slow reactions	Fast reactions
Rusting of iron	Double displacement reactions
Fermentation of sugar	Precipitation reactions
Weathering of rocks	Transmission of nerve impulses in our body
Digestion of food	Contraction of muscles
	Combustion
	Femtochemical reactions

Examples of chemical reactions

Example 1

How many times will increase rate of reaction when we increase temperature from 50oC to 80oC? Temperature coefficient of rate of the reaction is 3.

Solution

$$\frac{r(T_1)}{r(T_2)} = \gamma^{\frac{T_2 - T_1}{10}} \qquad r(T_2) = r(T_1) \cdot \gamma^{\frac{T_2 - T_1}{10}} \qquad r(T_2) = r(T_1) \cdot 3^{\frac{80-50}{10}}$$

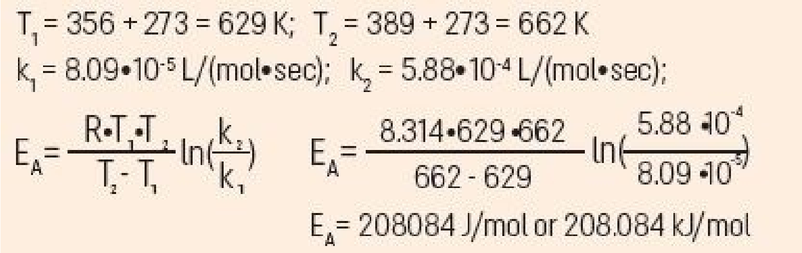
$$r(T_2) = r(T_1) \cdot 3^3 \qquad r(T_2) = r(T_1) \cdot 27$$

Answer: Rate of reaction increases 27 times.

Example 2

Calculate activation energy of the decomposition reaction of hydrogen iodide if rate constants at 356oC and 389oC are 8.09•10-5 L/(mol•sec) and 5.88•10-4 L/(mol•sec) respectively.

Solution:



$T_1 = 356 + 273 = 629\ K;\ \ T_2 = 389 + 273 = 662\ K$

$k_1 = 8.09 \cdot 10^{-5}\ L/(mol \cdot sec);\ \ k_2 = 5.88 \cdot 10^{-4}\ L/(mol \cdot sec);$

$$E_A = \frac{R \cdot T_1 \cdot T_2}{T_2 - T_1} \ln\left(\frac{k_2}{k_1}\right) \qquad E_A = \frac{8.314 \cdot 629 \cdot 662}{662 - 629} \ln\left(\frac{5.88 \cdot 10^{-4}}{8.09 \cdot 10^{-5}}\right)$$

$E_A = 208084\ J/mol$ or $208.084\ kJ/mol$

Literacy

1. What is the branch of chemistry which studies rate and mechanism of chemical reactions?

2. What are the units of following:

a) rate and b) rate constant of chemical reaction?

3. The decomposition of hydrogen bromide,

2HBr(g) → 2H2(g) + Br2(g)

has rate constants of 7.8 • 10-8 L/(mol•s) at 500 K and 2.1 •10-4 L/(mol•s) at 700 K. Find activation energy.

4. The reaction 2NO2(g) →2NO(g) + O2(g) has an EA of 1.7•103

kJ/mol and a rate constant of 5.2 • 10-3 L/(mol•s) at 500 K. What is the rate constant at 300 K?

5. For a reaction with a given E_A, how does an increase in T affect the rate? For a reaction at a given T, how does a decrease in EA affect the rate?

Terminology

- threshold - шекті / порог;
- respectively - сәйкесінше / соответственно;

6.4 CATALYSIS

Why is there a strong smell of gas coming from automobile exhaust?

You will:

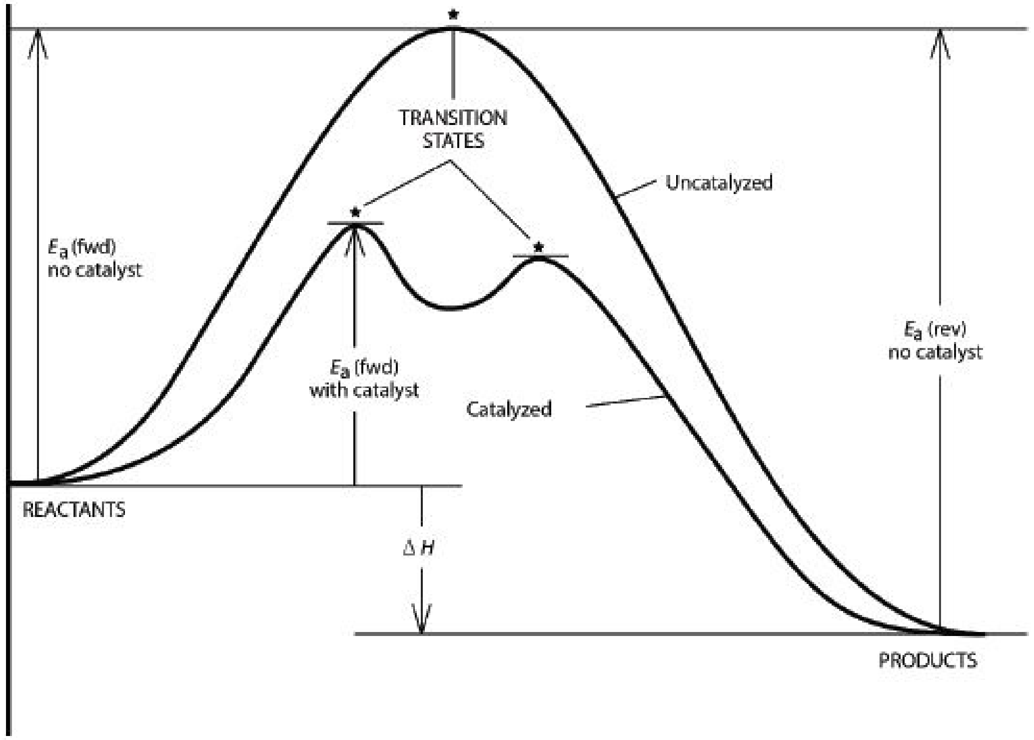
- understand what is catalysis;
- distinguish between homogeneous and heterogeneous catalysis;
- explain the action mechanism of catalysts;
- experimentally study the effect of various catalysts on the rate of decomposition of hydrogen peroxide.

Catalysis is a changing of rate of reaction by using catalyst. A catalyst is a substance that increases the rate of a reaction without being consumed during it. Catalyst changes the reaction path by decreasing the activation energy. For example, MnO2 catalyses the following reaction so as to increase its rate considerably.

$$2KClO_{3(s)} \xrightarrow{MnO_2} 2KCl_{(s)} + 3O_{2(g)}$$

The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown below:



Reaction energy diagram for a catalyzed and an uncatalyzed process.

It is clear from Arrhenius equation that lower the value of activation energy faster will be the rate of a reaction. A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction.

It catalyses the spontaneous reactions but does not catalyse nonspontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

Types of catalysis

There are three main types of catalysis: homogeneous and heterogeneous. It is important that you remember the diff erence between this two terms. In a homogeneous catalysis the catalyst is present in the same phase as reactants. For example production of SO3 by oxidation of SO2 in the industrial preparation of H2SO4. NO2 is used as a catalyst. All substances are in gaseous phase:

$$\begin{array}{c} 1.\ SO_{2(g)} + NO_{2(g)} \rightarrow SO_{3(g)} + NO_{(g)} \\ 2.\ NO_{(g)} + 1/2O_{2(g)} \rightarrow NO_{2(g)} \\ \hline SO_{2(g)} + 1/2O_{2(g)} \rightarrow SO_{3(g)} \end{array}$$

Heterogeneous catalysis involves the use of a catalyst in a different phase from the reactants. Usually solid catalyst used in gaseous or liquid phases. For example using V2O5 catalyst in the production of H2SO4 (Contact Process):

$$SO_{2(g)} + 1/2O_{2(g)} \rightarrow SO_{3(g)}$$

Efficiency of heterogeneous catalysts is greater than homogeneous. And if rate of reaction in the homogeneous catalysis depends on concentration of the catalyst, in the heterogeneous catalysis depends on specific surface area.

Activated carbon used as the catalyst for the catalytic synthesis of benzene

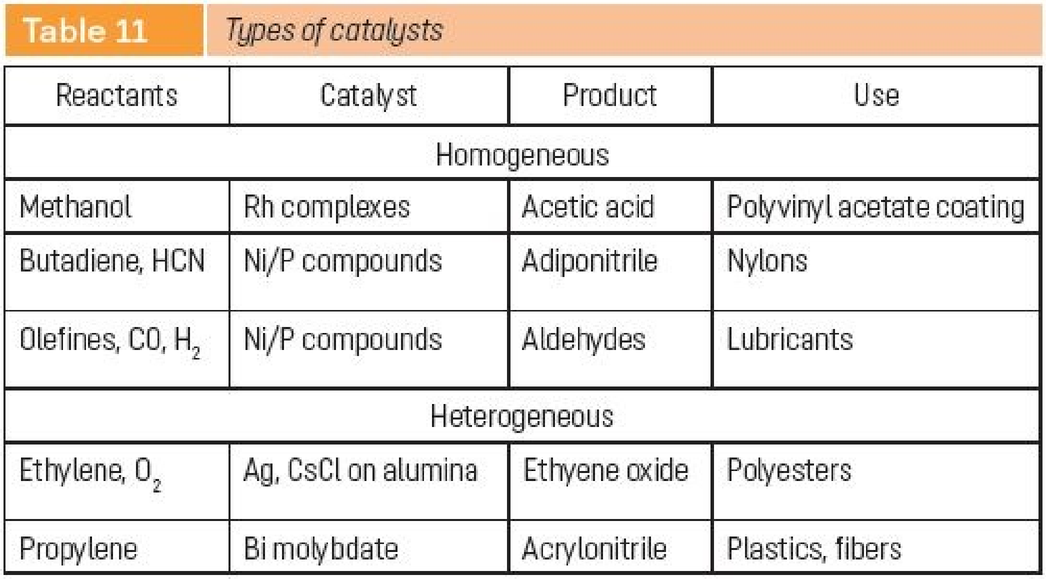


Table 11 *Types of catalysts*

Reactants	Catalyst	Product	Use
Homogeneous			
Methanol	Rh complexes	Acetic acid	Polyvinyl acetate coating
Butadiene, HCN	Ni/P compounds	Adiponitrile	Nylons
Olefines, CO, H_2	Ni/P compounds	Aldehydes	Lubricants
Heterogeneous			
Ethylene, O_2	Ag, CsCl on alumina	Ethyene oxide	Polyesters
Propylene	Bi molybdate	Acrylonitrile	Plastics, fibers

Keep in mind

“Homo” = Same

“Hetero” = Different

Chemfact

There are only four institutes of catalysis in the world: in Russian Federation, France, Japan and Republic of Kazakhstan.

Chemfact

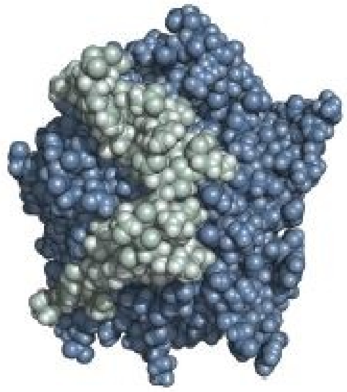
Dmitriy Vladimirovich SOKOLSKIY (1910-1987)

Chemist, doctor of chemical sciences, professor (1949), academician of Kaz SSR (1951), honored worker of science of Kaz

SSR (1960), Hero of Socialist labor (1969), laureate of the Kaz SSR State Prize (1974), honorable doctor of Budapest polytechnical University (1975), discovered the theory of optimization hydrogenation of catalyst. Worked in Kazakh State University: institute of organic catalysis and electrochemistry.

Chemfact

Enzymes play significant role in the biological processes. We can say that enzymes are biological catalysts.



Literacy

1. Identify homogeneous and heterogeneous catalysis

2. Which of the following statements are true?

- - Catalysts do not alter the enthalpy change of the reaction.
- - Catalysts which are in the same phase as the reactants are called heterogeneous catalysts
- - Important heterogeneous catalysts include Ni, Pt, Rh metals.
- - Catalysts do not take part in the reactions they speed up

Terminology

- enzyme - фермент / фермент
- considerably - айтарлықтай / значительно;
- specific surface area - меншікті беттік аудан / удельная поверхность

QUESTIONS AND PROBLEMS

1. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Express the rate in terms of changes in $[H_2]$, $[Cl_2]$ and $[HCl]$ with time.

When $[Cl_2]$ is decreasing at 0.12 mol/(L×s), at what rate $[HCl]$ increasing?

2. Balance the following equation and express the rate in terms of the change in concentration with time for each substance:

$N_2(g) + H_2(g) \rightarrow NH_3(g)$

How fast is $[H_2]$ decreasing when $[NH_3]$ is decreasing at a rate of 0.8×10^{-3} mol/(L×s)?

3. Write the rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of the products:

- $Cl_2(g) + I^-(aq) \rightarrow 2Cl^-(aq) + I_2(l)$
- $H_2S(g) + SO_2(g) \rightarrow S(s) + H_2O(l)$
- $CO(g) + H_2O(g) \rightarrow HCOOH(g)$

4. The trimerization of acetylene C_2H_2 to benzene C_6H_6 is a first-order reaction with a rate constant of 2.3×10^{-5} 1/s at 550°C:

3C2H2(g) → C6H6(l)

Calculate the half-life of the reaction in minutes.

5. Find the rate relationship of reactants and products for the given reaction.

H2O2(l) → H2O(l) + O2(g)

6. In a 1 L container, CO and H2O gases react with each other. After 20 seconds, 0.4 mol of HCOOH is produced. Express and find the reaction rate in terms of reactants and products.

CO(g) + H2O(g) → HCOOH(g)

7. If 5.2×10–3 mol/L NH3 is consumed in 2.5 minutes according to the reaction below;

4NH3(g) + 5O2(g) → 4NO(g) + 6H2O(g)

what will be the rate of formation of NO(g) and H2O(g) in mol/(L×s)?

8. For each of the following reactions, use the given rate law to determine the reaction order with respect to each reactant and the overall order:

- CO(g) + O2(g) → CO2(g); rate=k[CO][O2]
- 4NH3(g) + 5O2(g) → 4NO(g) + 6H2O(g); rate=k[NH3]4[O2]5

7
CHAPTER

EQUILIBRIUM

CHAPTER 7: EQUILIBRIUM

7.1 CHEMICAL EQUILIBRIUM

Suppose that you have 5 kg of ice (at -5°C and 1 atm). What happens if you increase the temperature to 0oC? Will all the ice melt, or will they stay intact and no liquid water is formed?

You will:

- know which metals are called alkali metals;
- know properties of alkali metals according to their atomic structure;
- know that oxides and hydroxides of alkali metals are bases.

In the previous chapter, we discussed the rate of reactions and the factors affecting reaction rates. We also learned that there is a relation between the concentration of reactants and the rate.

In the stoichiometry of chemical reactions, it is assumed that the reaction goes to completion, so that one of the reactants is consumed. However, many reactions do not go to completion, but rather establish an equilibrium. In this chapter, we will study equilibrium reactions.

Physical equilibrium

Water evaporates at all temperatures above 0°C. Thus, water in a open container evaporates, and in time no liquid water molecules remain in the container. However, water in a closed container does not exhaust, although evaporation takes place continuously.

Evaporation of liquid water forms water vapor which is a gas in the closed container. After a while, water vapor molecules start collisions with each other and with the water's surface, then they turn into water. Therefore, evaporation and condensation are reversible processes in a closed container. Reversible processes are represented by "↔". Irreversible processes are represented by "→".

$$H_2O(l) \leftrightarrow H_2O(g)$$

At the beginning, the rate of evaporation of water is higher than the rate of water formation. However, the rate of evaporation of water and the rate of condensation of water becomes equal after a period of time. At this time, the system is at equilibrium. Such an equilibrium is called physical equilibrium.

At equilibrium, the amounts of water vapor and water remain constant. However, evaporation and formation of water occur continuously on a microscopic scale.

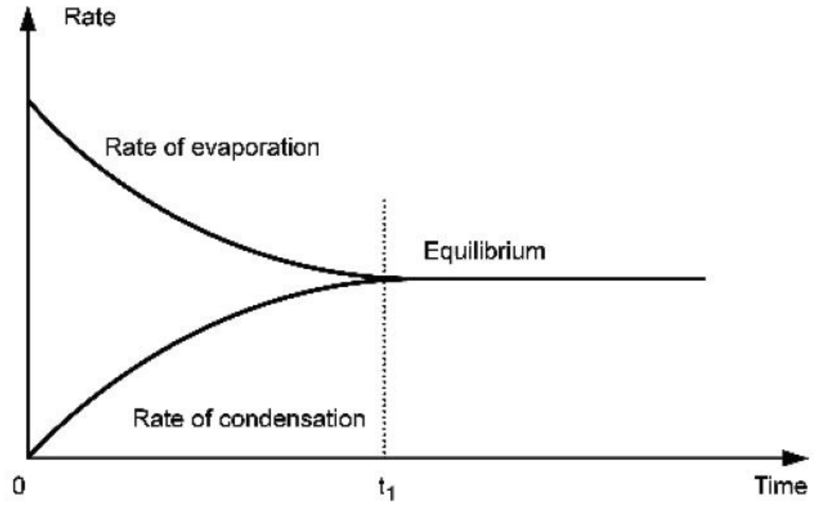
Thus, this type of equilibrium is called a dynamic equilibrium.

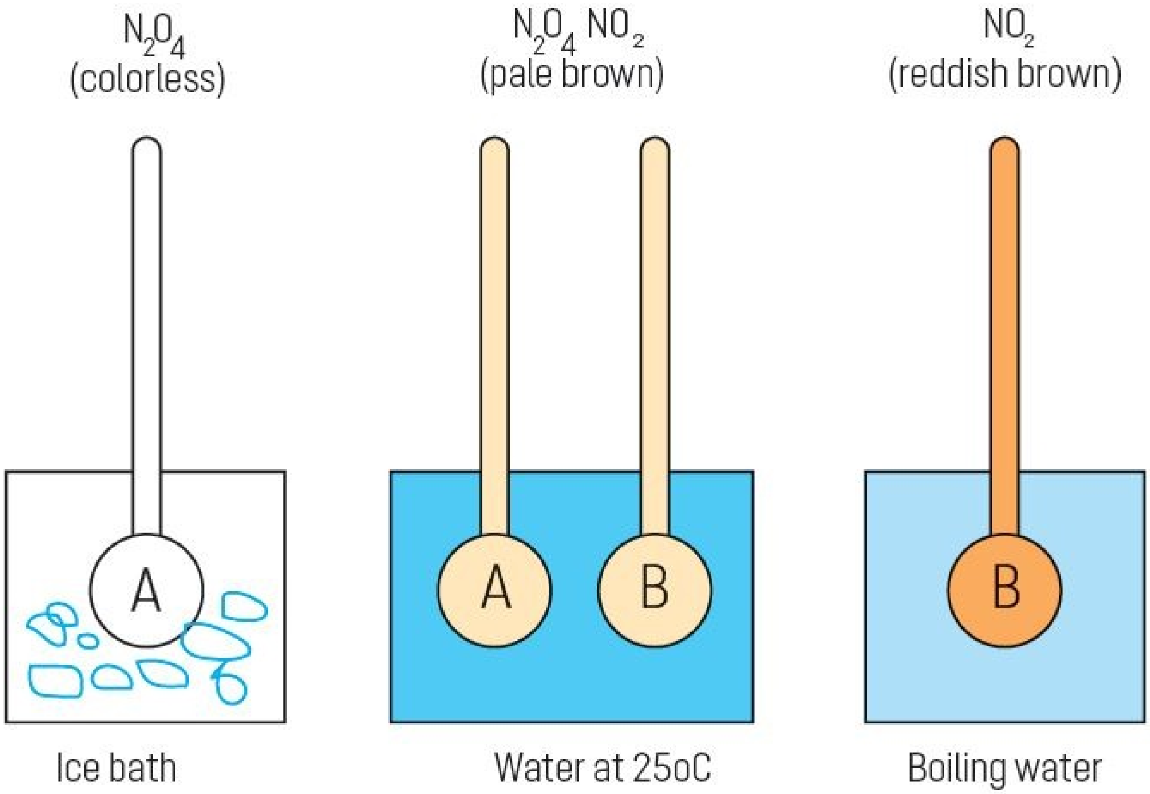
Chemical equilibrium

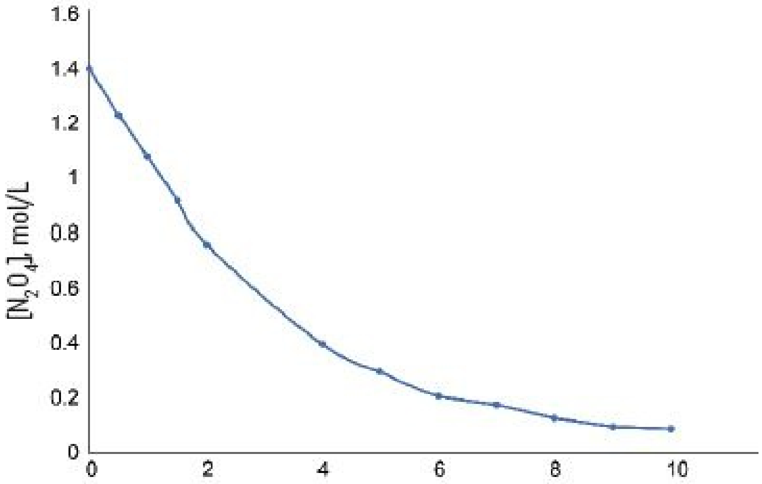
When a sample of N2O4, a colorless and poisonous gas, is placed in a closed container, a reddish-brown color develops due to the presence of nitrogen dioxide, NO2. As soon as some NO2 is formed, the reverse reaction can occur simultaneously with the forward reaction.

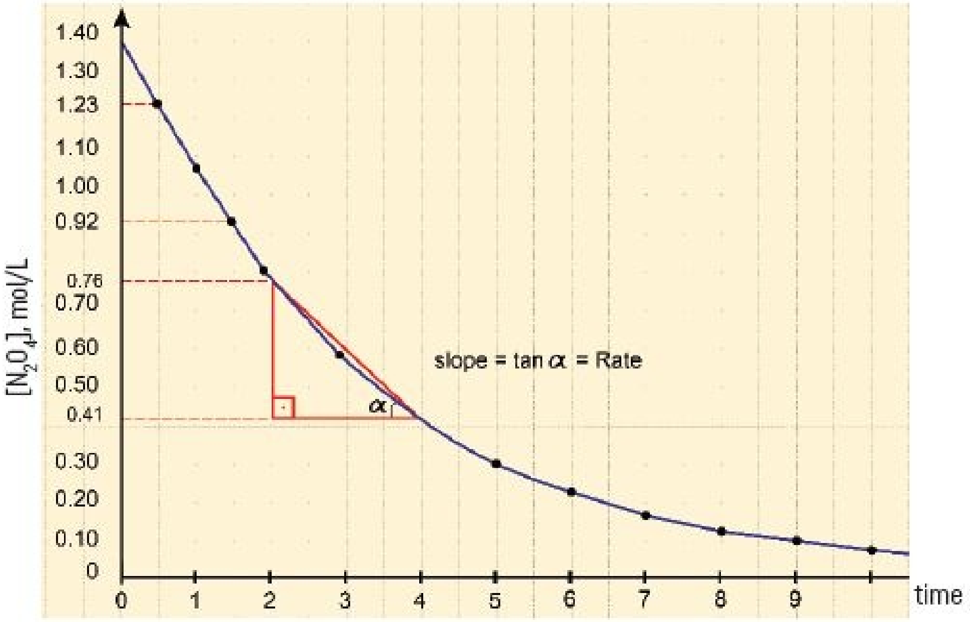
$$\mathrm{N2O4(g)} \leftrightarrow \mathrm{2NO2(g)}$$

When the rate of evaporation is equal to the rate of condensation, the dynamic equilibrium is established




N_2O_4
(colorless)
N_2O_4 NO_2
(pale brown)
NO_2
(reddish brown)
A
A
B
B
Ice bath
Water at 25oC
Boiling water


1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
$[N_2O_4]$, mol/L
0
2
4
6
8
10



As times passes, the rate of forward and reverse reactions become equal. At this point, a dynamic equilibrium is established. At equilibrium, amounts of reactants and products remain constant. Therefore, the color of the mixture does not change.

There are fundamental aspects of a chemical equilibrium state:

1. It exhibits no visible evidence of change.

2. It is reached through spontaneous change.

3. Forward and reverse reactions take place continuously.

4. It shows a dynamic balance between forward and reverse reactions.

Keep in mind

When two opposing chemical reactions occur at the same rate, the system is in a state of dynamic equilibrium, with concentrations of reactants and products remaining constant.

Literacy

1. What does a dynamic equilibrium mean? Can you think of a concept of “idle” or “inactive” equilibrium?

2. Water boils at 100oC. Although, at 25^{O}C water spilled on the floor disappears after couple of hours. Explain this phenomenon by using the concept of equilibrium.

3. Distinguish between a physical equilibrium and a chemical equilibrium:

- - melting of ice and freezing of water
- - formation of ammonia from nitrogen and hydrogen
- - evaporation-condensation of water
- - 2SO2 + O2 ↔ 2SO3
- - dissolution of excess sodium chloride in water

4. Why is BeCO3 stored in carbon dioxide atmosphere?

Chemfact

Beryllium carbonate BeCO3 is the least stable alkaline earth metal carbonate. To slow down its decomposition, we store it in a carbon dioxide atmosphere (reverse equilibtrium).

BeCO3 ↔ BeO + CO2

Research time

Open in browser Phet. Reversible Reactions.

Watch a reaction proceed over time. How does total energy affect a reaction rate?

Terminology

-
- equilibrium - тепе-теңдік / равновесие
- intact - бұзылмаған / неповрежденный
- simultaneous - бір мезетте / одновременное

7.2 FACTORS AFFECTING EQUILIBRIUM. LE CHATELIER'S PRINCIPLE

If a system is in a state of equilibrium on earth, would they be the same on the moon with the same pose?

You will:

- predict the effect of changes in temperature, concentration and pressure on chemical equilibrium;
- explain why the catalyst provides the fast establishment of equilibrium, but does not shift it;
- experimentally explore effects of different factors on shifting of the equilibrium

If a chemical system at equilibrium is disturbed by a change of concentration, pressure, or temperature, the system tends to counteract this change in order to reestablish a new equilibrium. In a chemical equilibrium, this principle is called Le Chatelier's principle.

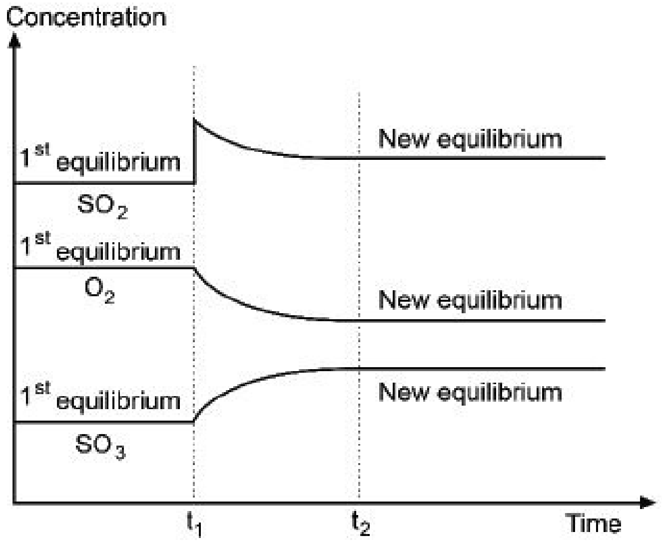
Effect of concentration change

In the given reaction,

$$2SO2(g) + O2(g) \leftrightarrow 2SO3(g)$$

if a small quantity of SO2 or O2 is added to the equilibrium mixture, the addition of these substances disturbs the equilibrium. Since the addition of SO2 or O2 increases the concentration of reactants, the reaction counteracts by decreasing the concentration of reactants. Thus, equilibrium shifts towards products to establish a new equilibrium.

If some amount of product, SO3, is added to the system, the concentration of product increases. Thus, the reaction shift s towards the reactants to decrease the concentration of products and to establish a new equilibrium state.



When SO_2 is added to the system, the first equilibrium system is disturbed and a new equilibrium state is established

Changes in the concentration of reactants or products will cause a shift to reestablish the equilibrium

Example 1

A gas mixture of N2, O2, and NO in a 1 L container at constant temperature has, n(N2) = 4 mol, n(O2) = 1 mol and n(NO) = 4 mol at equilibrium. When 3 mol of O2 are added to the container, in time, a new equilibrium is established.

N2(g) + O2(g) ↔ 2NO(g)

What will be the mole number of NO at the new equilibrium?

Solution:

First, the Kc value is calculated at the given condition. Since the volume is 1 L, for the concentrations

s

$$C = \frac{n}{V} \qquad C = \frac{n}{1} \qquad C = n \qquad K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{4^2}{4 \times 1} = 4$$

According to Le Châtelier's principle, when 3 mol of O2 is added to the container, the equilibrium will shift toward the product side by decreasing the concentrations of reactants.

$$N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$$

1st equilibrium:	4 mol	1 mol	4 mol
Effect:	-	+3 mol	-
Change:	-x	-x	+2x
New: equilibrium:	(4 - x) mol	(4 - x) mol	(4 + 2x) mol

$$K_c = \frac{(4+2x)^2}{(4-x)(4-x)} \qquad \sqrt{4} = \sqrt{\frac{(4+2x)^2}{(4-x)^2}} \qquad 2 = \frac{4+2x}{4-x} \qquad x = 1$$

$n(NO) = 4 + 2x = 4 + 2 \cdot 1 = 6$ mol.

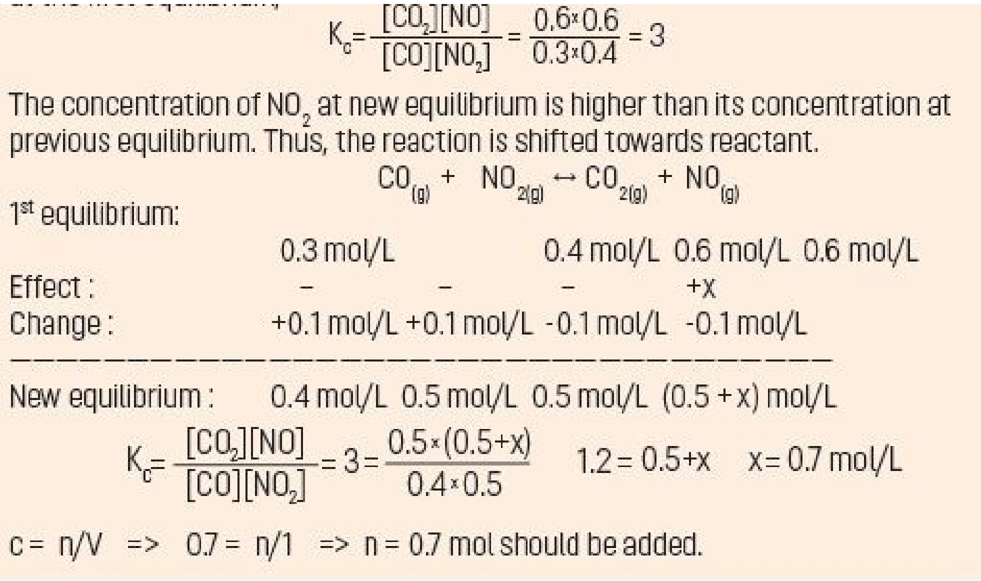
Example 2

CO(g) + NO2(g) ↔ CO2(g) + NO(g),   V = 1 L

There are 0.3 mol of CO, 0.4 mol of NO2, 0.6 mol of CO2 and 0.6 mol of NO at equilibrium. How many moles of NO should be added to increase the mole number of NO2 to 0.5 at new equilibrium?

Solution:

The Kc value for the reaction is calculated by the concentrations of the substances at the first equilibrium,



$$K_c = \frac{[CO_2][NO]}{[CO][NO_2]} = \frac{0.6 \cdot 0.6}{0.3 \cdot 0.4} = 3$$

The concentration of NO_2 at new equilibrium is higher than its concentration at previous equilibrium. Thus, the reaction is shifted towards reactant.

	$CO_{(g)}$ +	$NO_{2(g)}$ ↔	$CO_{2(g)}$ +	$NO_{(g)}$
1st equilibrium:	0.3 mol/L	0.4 mol/L	0.6 mol/L	0.6 mol/L
Effect :	–	–	–	+x
Change :	+0.1 mol/L	+0.1 mol/L	-0.1 mol/L	-0.1 mol/L
New equilibrium :	0.4 mol/L	0.5 mol/L	0.5 mol/L	(0.5 + x) mol/L

$$K_c = \frac{[CO_2][NO]}{[CO][NO_2]} = 3 = \frac{0.5 \cdot (0.5+x)}{0.4 \cdot 0.5} \qquad 1.2 = 0.5 + x \qquad x = 0.7\ mol/L$$

c = n/V => 0.7 = n/1 => n = 0.7 mol should be added.

Effect of pressure (volume changes)

Change in volume alters the concentrations of gas reactants and gas products. When the volume of the system decreases; the reaction shifts to the side having the smaller number of coefficients of gases in the reaction equation to decrease the effect of change in volume, according to Le Châtelier's principle.

When the volume of the system increases, the reaction shifts to the side where the total number of gas coefficients in the balanced equation is larger. Consider the effect of decrease in volume on a mixture equilibrium of NO_2 and N_2O_4.

$$2NO_2(g) \leftrightarrow N_2O_4(g)$$

When the volume of the system is decreased, the equilibrium shifts toward the N_2O_4 because the coefficient of the product is smaller than that of the reactant, according to balanced reaction equation. When the volume of the system is increased, the equilibrium shifts toward the NO_2. The equilibrium reactions in which the total numbers of the coefficients of gases in reactants and products are equal are not influenced by volume changes. For example;

$$H_2(g) + Cl_2(g) \leftrightarrow 2HCl(g)$$

$$N_2(g) + O_2(g) \leftrightarrow 2NO(g)$$

are not affected by changing the volume.

For a heterogeneous equilibrium, the effect of volume is predicted by counting the number of moles of gas indicated on each side of an equation.

$$FeO(s) + CO(g) \leftrightarrow Fe(s) + CO_2(g)$$

The above equilibrium reaction is unaffected by volume change since the total number of coefficients of gases on each side of the reaction equation are equal.

Pressure of a gas is inversely proportional to volume. When the volume of a gas increases, the pressure of the gas decreases. When the volume of a gas decreases, the pressure of the gas increases. Thus, change in pressure at constant temperature affects the equilibrium reaction conversely in respect to volume change.

The change in pressure and volume of a system that involves only liquids and solids can be ignored.

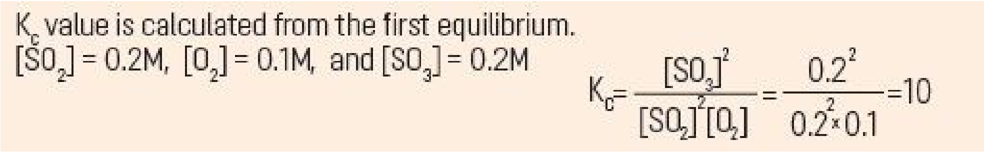
Example 3

2SO2(g) + O2(g) ↔ 2SO3(g),   V = 1 L

There are 0.2 mol of SO2, 0.1 mol of O2, and 0.2 mol of SO3 gases in a 1 L container at equilibrium. When the volume of the container is increased at a constant temperature, and 0.3 mol of SO2 gas is found in the container at a new equilibrium.

What will be the new volume of the container?

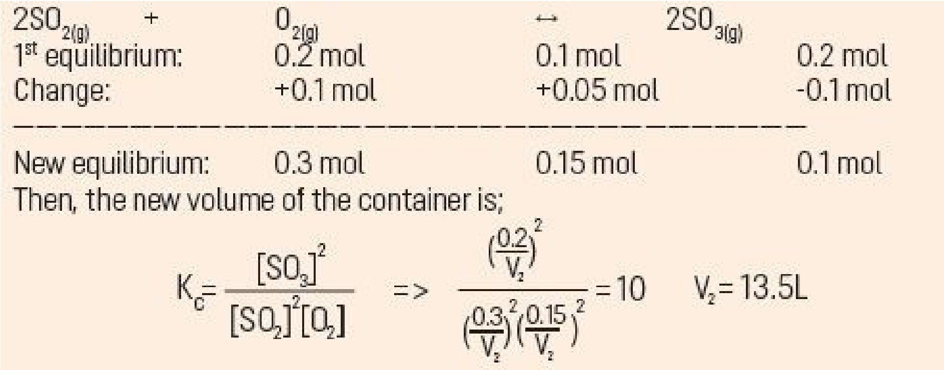
Solution:



K_c value is calculated from the first equilibrium.
$[SO_2] = 0.2M$, $[O_2] = 0.1M$, and $[SO_3] = 0.2M$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{0.2^2}{0.2^2 \times 0.1} = 10$$

When the volume is increased (the pressure decreases), the system shifts to the side having the larger number of coefficients of gases in the reaction equation. Thus, reaction shifts to the reactants.



$2SO_{2(g)}$ +	$O_{2(g)}$	↔	$2SO_{3(g)}$
1st equilibrium:	0.2 mol	0.1 mol	0.2 mol
Change:	+0.1 mol	+0.05 mol	-0.1 mol
New equilibrium:	0.3 mol	0.15 mol	0.1 mol

Then, the new volume of the container is;

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \Rightarrow \frac{\left(\frac{0.2}{V_2}\right)^2}{\left(\frac{0.3}{V_2}\right)^2\left(\frac{0.15}{V_2}\right)^2} = 10 \qquad V_2 = 13.5L$$

Effect of temperature

In order to understand the effect of temperature change on an equilibrium system, we should know the heat effect on a reaction. Let's consider the following reaction.

$$N_2O_4(g) + 58\ kJ \leftrightarrow 2NO_2(g)$$

The forward reaction is endothermic, and the reverse reaction is exothermic, according to the Le Châtelier's principle. If we change the temperature of the system, it will shift in a way that will decrease the effect of the change. If the temperature of the system is raised, the equilibrium will proceed to the right (products) to decrease the temperature, according to the Le Châtelier's principle. If the reaction mixture is cooled down, the equilibrium will shift to the left (reactants) to increase the temperature.

Increasing temperature shifts equilibrium to the right

$$N2(g) + 3H2(g) \leftrightarrow 2NH3(g) + 92 \text{ kJ}$$

In the above reaction, the forward reaction is exothermic, and the reverse reaction is endothermic. If the system is heated (the temperature raised), the equilibrium will shift to the left to counteract the effect of the change.

The equilibrium constant, Kc or Kp, change only by altering the temperature.

Table 12 *In an exothermic reaction, increasing temperature raises the concentrations of reactants. Thus, it decreases the K_c value*

Equilibrium Reaction	K_c	Temperature (°C)
$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$ + heat	$2.66 \cdot 10^{-2}$	350
$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$ + heat	$6.59 \cdot 10^{-3}$	450
$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$ + heat	$2.37 \cdot 10^{-3}$	727
$2HI_{(g)}$ + heat $\leftrightarrow H_{2(g)} + I_{2(g)}$	$1.5 \cdot 10^{-2}$	350
$2HI_{(g)}$ + heat $\leftrightarrow H_{2(g)} + I_{2(g)}$	$1.8 \cdot 10^{-2}$	425
$2HI_{(g)}$ + heat $\leftrightarrow H_{2(g)} + I_{2(g)}$	$2.2 \cdot 10^{-2}$	490

Effect of catalyst

Catalyst does not affect the equilibrium constant and the equilibrium reaction. It only affects the rates of forward and reverse reactions. Thus, a catalyst causes an equilibrium system to reach equilibrium in a shorter time.

Manganese dioxide acts as a catalyst for the decomposition of hydrogen peroxide

Literacy

1. The above reaction is in equilibrium in a container. The partial pressures of NO2 and N2O4 are 0.2 atm and 1.6 atm, respectively, at equilibrium. If, at the same temperature, the volume of a container is increased and the total pressure on that container is found to be 2.2 atm at a new equilibrium, what is the partial pressure of NO2 gas at this new equilibrium?

$2NO_2(g) \leftrightarrow N_2O_4(g)$

Answer : 1 atm

2. Use Le Chatelier’s principle to predict how each of the following changes would affect this equilibrium

$2CH_4(g) \leftrightarrow C_2H_2(g) + 3H_2(g)$

a. adding C2H2 to the system

b. removing H2 from the system

c. removing CH4 from the system

3. How would decreasing the volume of the reaction vessel affect these equilibria?

a. 2CH4(g) ↔ C2H2(g) + 3H2(g)

b. CO(g) + H2O(g) ↔ CH3OH(g)

c. N2(g) + 3H2(g) ↔ NH3(g)

d. 2SO3(g) + CO2(g) ↔ CS2(g) + 4O2(g)

e. 2SO2(g) + O2(g) ↔ 2SO3(g)

Terminology

- affecting factors – әсер етуші факторлар / влияющие факторы
- catalyst – катализатор /катализатор
- established – орнау /установлено

7.3 THE EQUILIBRIUM CONSTANT EXPRESSION. CHEMICAL EQUILIBRIUM IN INDUSTRY

How does the value of an equilibrium constant relate to the relative quantities of reactants and products at equilibrium?

You will:

- compose equilibrium constant expression;
- predict the affecting factors on the equilibrium constant;
- perform calculations related to the equilibrium constant;
- explain the role of chemical equilibrium shift for increasing the yield of a product in the chemical industry using the example of the Haber process and the oxidation of sulfur oxide and nitrogen.

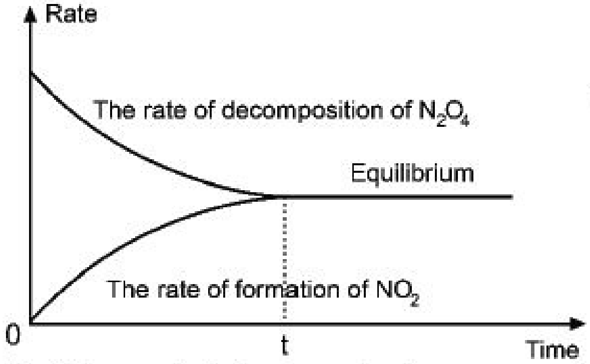
At equilibrium, the rate of forward and reverse reactions are equal. For the system:

N2O4(g) ↔ 2NO2(g)

The forward (1st) and reverse (2nd) rate expressions are,

$$\begin{aligned} r_1 &= k_1 \times [N_2O_4] \\ r_2 &= k_2 \times [N_2O_4]^2 \end{aligned}$$

Since the rate of N2O4 decomposition and the rate of NO2 formation are equal at equilibrium.



Equilibrium reached when forward and reverse rates of the reaction are equal

The equation; $r_1 = r_2$ can be written as

$$k_1 \times [N_2O_4] = k_2 \times [N_2O_4]^2$$

$$\frac{k_1}{k_2} = \frac{[NO_2]^2}{[N_2O_4]}$$

Since k1 and k2 are constants; a new constant can be derived from them. It is named as an equilibrium constant in terms of concentration, and is symbolized as “Kc”.

$$\frac{k_1}{k_2} = K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

In general, a Kc expression is written as

$$K_c = \frac{[\text{products}]}{[\text{reactants}]}$$

Solid and liquid substances are not represented in a Kc expression, since their concentrations do not vary in the course of reaction. For example,

C(s) + CO2(g) ↔ 2CO(g)

the equilibrium expression of the reaction is

$$K_c = \frac{[CO]^2}{[CO_2]}$$

Example 1

Ammonia can be produced from hydrogen and nitrogen,

$$N2(g) + 3H2(g) \leftrightarrow 2NH3(g)$$

Write the equilibrium expression for this reaction.

Solution:

$$K_c = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

The relation between Kc and Kp

For the reaction,

$$aA(g) + bB(g) \leftrightarrow cC(g) + dD(g)$$

relation between Kp and Kc is as follows,

$$Kp = Kc \cdot (RT)\Delta n$$

where Δn - coefficient differences of gaseous substances.

$$\Delta n = (c + d) - (a + b)$$

if Δn = 0, then; Kp = Kc

The units for Kc and Kp change with different reactions.

Example 2

$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

Write the equation relating Kc and Kp.

Solution:

$\Delta n = 2 - (1+3)$ then $\Delta n = -2$

$$K_p = K_c \times (RT)^{\Delta n} \Rightarrow K_p = K_c \times (RT)^{-2} \Rightarrow K_p = K_c / (RT)^2$$

Example 3

$$2NO(g) + 2H_2(g) \leftrightarrow N_2(g) + 2H_2O(g)$$

0.2 mol of NO, 0.1 mol of H2, 0.1 mol N2, and 0.4 mol of H2O exist in a 1 L container at equilibrium at 127°C. Find Kp and Kc of equilibrium reaction at 127°C.

Solution:

$$\begin{array}{cccc} 2NO_{(g)} & + 2H_{2(g)} \leftrightarrow & N_{2(g)} & + 2H_2O_{(g)} \\ 0.2\,M & 0.1\,M & 0.1\,M & 0.4\,M \end{array}$$

$$K_c = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{0.1 \times 0.4^2}{0.2^2 \times 0.2^2} = 40$$

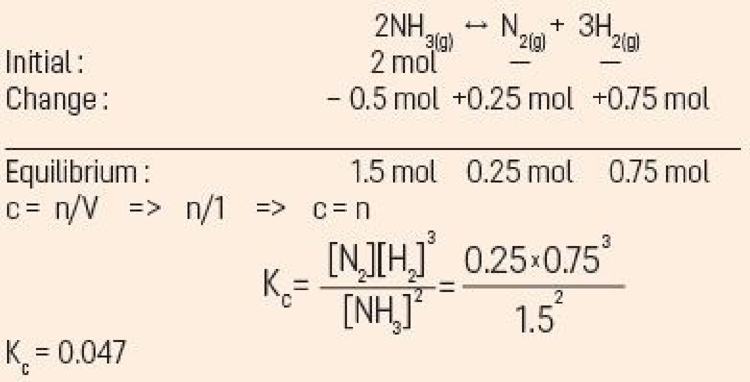
$$\Delta n = (1+2) - (2+2) = -1 \quad \text{and} \quad T = 273 + 127 = 400\,K$$
$$K_p = K_c \times (RT)^{\Delta n} = 40 \times (0.082 \times 400)^{-1}$$
$$K_p = 1.22$$

Example 4

$$2NH3(g) \leftrightarrow N2(g) + 3H2(g)$$

The reaction starts with 2 mol of NH3 in 1 L container. When 25 percent of NH3 decomposes into N2 and H2, the reaction establishes an equilibrium. What is the value of Kc?

Solution:



	$2NH_{3(g)}$ ↔	$N_{2(g)}$ +	$3H_{2(g)}$
Initial :	2 mol	—	—
Change :	− 0.5 mol	+0.25 mol	+0.75 mol
Equilibrium :	1.5 mol	0.25 mol	0.75 mol

c = n/V => n/1 => c = n

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{0.25 \times 0.75^3}{1.5^2}$$

$K_c = 0.047$

Keep in mind

Like in the case of Kc and Kp expressions, liquid and gas species are not included in the calculation of Δn.

Literacy

1. $H2(g) + F2(g) \leftrightarrow 2HF(g)$

The reaction starts with 2 mol of HF in a 5 L container.

When the equilibrium is established and the temperature is decreased to the initial temperature, the Kc value is found to be 100. What are the equilibrium concentrations of substances?

Answer : [HF] = 0.33 M,

[H2] = [F2] = 3.3•10-2 M

2. The reaction:

H2(g) + I2(g) ↔ 2HI(g)

occurs in a 2 L container at 127 °C. At equilibrium, 0.4 mol of H2, 0.1 mol of I2, and 0.3 mol of HI are found in the container. Find the values of Kc and Kp.

Answer : Kc = Kp = 2.25

3. Write the equilibrium constant expressions for the following reactions in terms of Kc and Kp.

a. N2(g) + 2O2(g) ↔ N2O4(g)

b. C(s) + CO2(g) ↔ 2CO(g)

c. H2(g) + I2(g) ↔ 2HI(g)

Answers: a. Kp = Kc•(RT)-2

b. Kp = Kc•RT c. Kp = Kc

Activity

The Haber process is the reaction of nitrogen and hydrogen to produce ammonia. The two elements nitrogen and hydrogen are reacted over an iron catalyst under 200 atm, at 450°C to produce ammonia.

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) + 92\ \text{kJ}$$

The reaction of H_2 with N_2 is an equilibrium reaction. The forward reaction is exothermic, meaning increasing the system’s temperature tends to shift the reaction toward the reactants.

QUESTIONS AND PROBLEMS

1. Write the reaction quotient, Qc, for each of the following reactions (unbalanced):

- - The decomposition of hydrogen iodide,

$HI(g) \leftrightarrow H_2(g) + I_2(g)$

- - The combustion of methane gas,

$CH_4(g) + O_2(g) \leftrightarrow CO_2(g) + H_2O(g)$

- - The combustion of ammonia,

$NH_3(g) + O_2(g) \leftrightarrow N_2(g) + H_2O(g)$

2. Write the equilibrium expression for following reactions:

- - $CO(g) + O_2(g) \leftrightarrow CO_2(g)$
- - $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- - $H_2O(l) \rightarrow H_2(g) + O_2(g)$

3. Write the equation relating Kc and Kp for following reactions:

- - $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
- - $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

4. Write the equation relating Kc and Kp for following reactions:

- - $CO(g) + H_2O(g) \leftrightarrow CH_3OH(g)$

- \- $H_2(g) + Br_2(g) \leftrightarrow 2HBr(g)$

5. $2NO(g) + 2H_2(g) \leftrightarrow N_2(g) + 2H_2O(g)$

0.2 mol of NO, 0.1 mol of H2, 0.1 mol N2, and 0.4 mol of H2O exist in a 1 L container at equilibrium at 127°C. Find the Kc and Kp of equilibrium reaction at 127°C.

6. $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$

0.1 mol of N2, 0.6 mol of H2, 0.4 mol of NH3 exist in a 1 L container at equilibrium at 57°C. Find the Kc and Kp of equilibrium reaction at 57°C.

7. $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$

The reaction starts with 4 mol of NH3 in 1L container. When 40% of NH3 decomposes into N2 and H2, the reaction establishes an equilibrium. What is the value of Kc?

8. $H_2(g) + F_2(g) \leftrightarrow 2HF(g)$

At 273 K in a 1 L container, 2 mol of H2 and 3 mol F2 react with each other. If Kc is 101.2, what are the equilibrium concentrations of reactants and products?

9. $CO(g) + H_2O(g) \leftrightarrow CH_3OH(g)$

The equilibrium constant of a given reaction is 6 at a given temperature. Is the system at equilibrium, if there exists a mixture of 0.1 mol of CO, 0.4 mol of H_2O, and 0.3 mol of CH_3OH in a 1 L container?

10. A gas mixture of N_2, O_2, and NO in a 1 L container at constant temperature has, n(N_2)= 4 mol, n(O_2)= 1 mol and n(NO)= 4 mol at equilibrium. When 3 mol of O_2 are added to the container, in time, a new equilibrium is established.

$N_2(g) + O_2(g) \leftrightarrow 2NO(g)$

What will be the mole number of NO at the new equilibrium?

11. $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$ V = 1 L

There are 0.2 mol of SO_2, 0.1 mol of O_2, and 0.2 mol of SO_3 gases in a 1 L container at equilibrium. When the volume of the container is increased at a constant temperature, and 0.3 mol of SO_2 gas is found in the container at a new equilibrium. What will be the new volume of the container?

12. What is Le Châtelier's principle?

13. What are the factors affecting an equilibrium system?

14. What is equilibrium constant? Which factors affect the equilibrium constant?

15. $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ $K_c=49$

The above reaction reaches equilibrium in

a 1.12 L container at 0°C. What will be the total pressure at equilibrium, if the system starts with 0.9M H_2 and 0.9M I_2 in the container?

16. PCl_5 molecule is decomposed in 22.4 L container at 273°C.

$PCl_5 \leftrightarrow PCl_3 + Cl_2$

When the system reaches equilibrium at the same temperature, there are 6.4 mol PCl_5, 3.2 mol PCl_3 and 3.2 mol of Cl_2 in the container. What is the Kp constant of the reaction?

8
CHAPTER

REDOX REACTIONS

CHAPTER 8: REDOX REACTIONS

8.1 OXIDATION-REDUCTION PROCESSES

What are oxidation and reduction, and why do they always occur together?

You will:

- write equations of redox reactions by oxidation number method;
- write equations of redox reactions by half equation method.

As you can remember from 9 grades, reactions which involve a transfer of electrons are called RedOx or Oxidation-Reduction reactions. Transfer of electrons can be easily detected by comparing oxidation numbers, or as we usually call them charges, of reactants and products. So, substances which lose electrons are called reducing agents and oxidizing agents gain that electrons.

Products of such reactions can be easily predicted; now we will try to understand how to “crack” these reactions.

To write products in RedOx reactions, first of all, we need to understand nature of reacting substances. For instance, a strong oxidizing agent will increase oxidation number of reducing agent to its maximum while weak one can't do so.

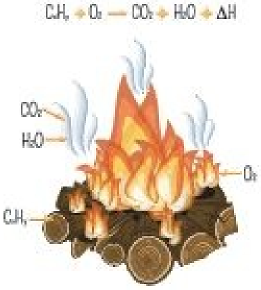
As an example we can take H2S, under the effect of strong oxidizers it will turn into H2SO4 (S-2 → S+6) and weak oxidizers will turn it into S ($S^{-2} \rightarrow S^{0}$). This is similar to reducers but they will show opposite effect.
Therefore, it necessary to list the most common oxidizers and reducers.

- Strong oxidizing agents: F2, O2, O3, H2O2, Cl2, HClO3, HNO3, HNO2, NO2, H2SO4 conc, Aqua regia, KMnO4, K2Cr2O7.
- Weak oxidizing agents: I2, bromine water (Br2 + H2O), SO2, Fe3+, HCl, etc.
- Strong reducing agents: alkali and alkaline earth metals, Al, H2, HI and iodides, HBr and bromides, H2S and sulfides, NH3, C, CO, Fe2+, Cr2+.
- Weak reducing agents: passive metals (Pb, Cu, Ag, Hg), HCl and chlorides, SO2, HNO2.

In order to write the chemical equation for RedOx reactions you need to use the following algorithm of actions:
1. Determine oxidizer and reducer. You can use the list of common oxidizers and reducers.
2. Determine resulting oxidation states of oxidizer and reducer after the reaction. Look at the example above with H2S.
3. Determine in which forms the reduced and oxidized compounds do exist. Don't forget that medium also affects the resulting products. For instance, Fe3+ in an acidic medium exist as salt Fe (III) while in a basic medium as Fe(OH)3.
4. Balance the reaction. You can use the oxidation-number method or half-equation method.

Let's consider some examples for better understanding the given algorithm of actions.

Monochromate and dichromate solutions



In combustion reactions oxidation state of carbon always changed

Example 1

Suggest products for reactions of iron with (a) chlorine gas and (b) hydrochloric acid. Balance the reactions.

Solution

a. Chlorine gas is a strong oxidizing agent that's why it will increase oxidation number of iron to its maximum state - Fe3+. Fe3+ exist as salt in a resulting product. Chlorine will turn to Cl- to its only possible state in reduction process. So the only product is FeCl3.

Fe(s) + Cl2(g) → FeCl3(s)

To balance the reaction you can use oxidation-number method (look at chapter 5 in 9 grade book):

2Fe(s) + 3Cl2(g) → 2FeCl3(s)

b. Hydrochloric acid is weak oxidizing agent so it will increase oxidation number of iron only to Fe2+. Fe2+ exist as salt in a resulting product. Hydrogen will turn to H2 to its only possible state in the reduction. So product are FeCl2 and H2. Balance the reaction by use of oxidation-number method:

Fe(s) + 2HCl(aq) → FeCl2(aq) + H2(s)

Half Equation method

In a Half Equation method transfer of electrons between atoms or ions under the effect of a medium is considered. This method also can be called as Ion-Electron method. In half reactions of oxidation and reductions processes, real states of substances are written. Strong electrolytes are written in ionic form while weak electrolytes and insoluble compounds in molecular form. To balance a number of hydrogen and oxygen atoms molecules of water H2O and ions H+ (in acidic medium) or OH- (in basic medium) are used. Half-equation is used only for aqueous solutions.

The most common half-reactions of some oxidizers:

1. a. MnO4- + 8H+ + 5e- → Mn2+ + 4H2O (acidic medium)

b. MnO4- + 2H2O + 3e- → MnO2 + 4OH- (neutral medium)

c. MnO4- + e- → MnO42- (basic medium)

2. a. NO3- + 2H+ + e- → NO2 + H2O (conc. acid with weak reducer)

b. NO3- + 4H+ + 3e- → NO + 2H2O (conc. acid with strong reducer)

c. NO3- + 10H+ + 8e- → NH4+ + 3H2O (dilute acid with strong reducer)

3. a. Cr2O72- + 14H+ + 6e- → 2Cr3+ + 7H2O (acidic medium)

b. CrO42- + 4H2O + 3e- → [Cr(OH)6]3- + 2OH- (basic medium)

These examples show us relationship between products of redox reactions and strength of oxidizers/reducers or medium characteristic.

Example 2

Suggest products for the following reaction. Balance the reaction by use of ion-electron method.

FeSO4(aq) + KMnO4(aq) + H2SO4(aq) →

Solution

The medium of a solution is acidic. KMnO4 will be reduced to Mn2+ while the only anion present in the solution is SO42-, so that Mn2+ will be in the form of MnSO4. Fe2+ will be oxidized to Fe3+, here also, only one salt is possible - Fe2(SO4)3. Now we need to add remaining spectator ion which is K+, salt is K2SO4. Chemical equation of the reaction is:

FeSO4(aq) + KMnO4(aq) + H2SO4(aq) → Fe2(SO4)3(aq) + MnSO4(aq) + K2SO4(aq)

For now, we can't tell where are the molecules of water, on the right side or left. It will become clear after we balance the reaction.

Let's write half-reactions:

There are two iron atoms on right side, so the oxidation half-reaction is:

2Fe+2 → 2Fe+3 + 2e-

The reduction half-reaction is:

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Next, sum up the two half-reactions, as follows:

$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ / 5

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ / 2

$10Fe^{2+} + 2MnO_4^- + 16H^+ \rightarrow 10Fe^{3+} + 2Mn^{2+} + 8H_2O$

Now it is clear that water molecules are on the right side. Finally, let's add remaining spectators ions:

$10FeSO_4(aq) + 2KMnO_4(aq) + 8H_2SO_4(aq) \rightarrow 5Fe_2(SO_4)_3(aq) + 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l)$

Keep in mind

Oxidation is process of losing electrons by atom or ion.

Reduction is process of gaining electrons by atom or ion.

Research time

Open in browser Tarnishing of silver.

What chemical exuded through the skin causes silver jewelry to tarnish?

What is the difference between corrosion and tarnishing of metals?

Chemfact

Redox reactions found their application many centuries ago. One of these examples is "Greek fire". It was created by Byzantines in the seventh century A.D. Greek fire could burn on water and so it found its application in naval battles to destroy enemy ships. The composition of the mixture remains unknown but some proposals were done. It said that Greek fire could contain petroleum, potassium nitrate, and possibly quicklime.

Literacy

1. Write chemical equations for reactions of iron (III) chloride and potassium iodide (a), iron (II) sulfide and oxygen gas (b). Predict products of reactions and balance them by use of an oxidation-number method.

2. Suggest products for the following reaction. Balance the reaction by use of ion-electron method.

Cu(s) + HNO3(aq)(conc) →

3. Suggest products for the following reactions. Balance the reactions by use of an oxidation-number method.

- - S(s) + NO2(g) →
- - KClO3(s) + HCl(aq) →

4. Suggest products for the following reactions. Balance the reactions by use of ion-electron method.

- - Mg(s) + HNO3(dil) →
- - K2Cr2O7(aq) + H2S(g) + H2SO4(dil) →

5. Suggest reactants for the following reactions. Assume that there are only two reactants. Balance the reactions by use of method more suitable for you.

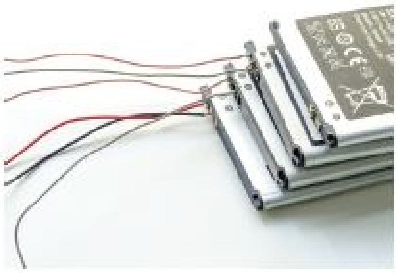
- → FeCl2(aq) + S(s) + HCl(aq)
- → I2(s) + NO(g) + H2O(l)
- → CuSO4(aq) + Br2(l) + SO2(g) +H2O(l)

Terminology

- electronegativity - элекртерістік / электроотрицательность;
- to insulate - оқшаулау / изолировать;
- sensitive - сезгіш / чувствительный;
- to restrict - шектеу қою / ограничить;
- refrigerator - тоңазытқыш / холодильник;
- insecticide - инсектицид / инсектицид.

8.2 STANDARD REDUCTION POTENTIAL

Potassium and sodium are much more abundant than lithium. So why is lithium used in batteries instead?



Lithium batteries

You will:

- explain term "standard electrode potential";
- use standard electrode potentials to predict possibility of the reaction.

Any oxidation or reduction half-reaction can be written in standard form:

$$Ox + ne^- \rightarrow Red$$

where Ox is an oxidizer and Red is a reduced form of Ox.

Such half-reactions can be characterized by a standard reduction potential, Eo. Unit of Eo is volt. The greater Eo is, the stronger is Ox as the oxidizing agent and the weaker Red as the reducing agent and vice versa.

Table 13 *Some half-reactions with their standard reduction potentials:*

Half-reaction	*E° (V)*
$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$	+0.80
$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$	+0.34
$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$	0.00
$Zn^{2+}_{(aq)} + 2e^{-} \rightarrow Zn_{(s)}$	-0.76
$Al^{3+}_{(aq)} + 3e^{-} \rightarrow Al_{(s)}$	-1.66

Let's look at our standard reduction potential table and see if it can help us to understand oxidizing and reducing agents.

Eo for the reduction half-reaction of hydrogen ion into hydrogen gas is equal to 0.00. Therefore, it can be seen why was chosen as the reference value. And it needs to mention that standard reduction potentials are always given for 25oC degree and 1 atm pressure.

Also, if we compare first half-reaction, where silver ion takes an electron to form solid silver, and half-reaction of reduction for aluminum it can easily be understood that silver is more likely to be reduced than aluminum. So, it can be supposed that aluminum is stronger reducer that silver. If you look at the list of strong and weak reducing agents from the previous lesson, you will find that our suggestion was right.

Activity

Elon Mask founded the company Tesla (company specializes in electric cars). Write the short text about the electric cars. Include the following information:

- - how do electric car work?
- - what are the benefits of electric cars?
- - what type of battery is used in electric cars?

Example 1

Can solid zinc reduce copper ion from its solution? If it can do what will be total potential for this reaction?

Solution

As we can see from the table above, the standard reduction potential of reduction half-reaction for copper ion is obviously more positive than that of zinc ion. So, copper ion is an oxidizing agent and will undergo reduction reaction while zinc will be reducing agent and it will be oxidized. However, our table contains only reduction half-reactions. Therefore we need to reverse reduction reaction for zinc to show it as an oxidation reaction. Since we reversed our half-reaction, we need to change the sign of Eo:

Oxidation: Zn(s) → Zn2+(aq) + 2e-

Eoox = +0.76 V

Reduction: Cu2+(aq) + 2e- → Cu(s)

Eored = +0.34 V

So, the answer to the first question is yes, zinc can reduce copper ion.

Let's move to the second question. To find total potential we just need to add two half-reactions, reduction and oxidation:

Overall reaction:

Zn(s) + Cu2+(aq) → Zn2+(aq) + Cu(s)

Eototal = Eoox + Eored = 0.76 + 0.34 = +1.10 V

Thus, the cell potential is the sum of potentials of oxidation and reduction halfreactions.

So, answer is Eocell = +1.10 V

For the half-reactions as

Men+ +ne- → Meo

Eo is called standard electrode potential. By value of these potentials, metals are arranged in order that you know from 8 grades as "Activity series of metals."

Li Rb K Ba Sr Ca Na Mg Al Mn Zn Cr Fe Cd Co Ni Sn Pb (H) Bi Cu Hg Ag Pt Au

Activity series characterises chemical properties of metals:

Metal is able to displace from the salt solutions those metals that stand in the activity series to the right of it. Metals that are located on the left side of hydrogen can displace it from its acid solutions.

Spontaneity of Redox Reactions

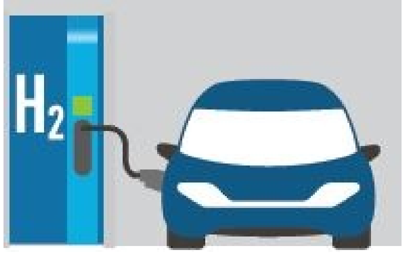
If the Eo cell value for a redox reaction is positive, the reaction will be spontaneous.

If the Eo cell value is negative, the reaction will not occur.

Chemfact

A fuel cell is a kind of voltaic cell that is designed for the continuous replenishment of the consumed reactants. A very common kind of fuel cell produces electricity directly from hydrogen and oxygen.

For this type of fuel cell, water is the product. In other words, hydrogen combines with oxygen and, as a result, produces energy in the form of heat and mechanical motion. In a fuel cell, the fuel is also oxidized, but the resulting energy takes the form of electricity. While fuel cells are obviously a cleaner energy resource than other types of fossil fuels, the storage of hydrogen is a big problem in their development. The hydrogen-oxygen fuel cell, a Proton Exchange Membrane (PEM) fuel cell, was primordially developed by General Electric between 1959 and 1982.



Example 2

Predict whether or not Zn2+ can oxidize Al(s) and calculate Eo for the reaction.

Solution

So, we know from Activity series of metals that Zn is standing to the right of Al. Therefore, Zn2+ can be displaced from its solution by Al or as we can say Zn2+ is able to oxidize Al.
Let's calculate Eo for the reaction and prove our suggestions.
The half-reactions are:
Oxidation: Al(s) → Al3+(aq) + 3e- 2
Eoox = +1.66 V
Reduction: Zn2+(aq) + 2e- → Zn(s) 3
Eored = -0.76 V

Cell: 2Al(s) + 3Zn2+(aq) → 2Al3+(aq) + 3Zn(s)
Eocell = +0.90 V
Since Eocell > 0, the reaction will occur towards the product side spontaneously. We was right.

Note: that half-cell potentials are not multiplied by their coefficients. It is because voltage is an intensive property. It doesn't matter how much of metal is involved, voltage always will be the same.

Example 3

Predict the spontaneity of reaction when a iron nail is dipped into HCl solution.
Fe(s) + 2HCl(aq) → FeCl2(aq) + H2(g)

Hint: you can find standard electrode potential of iron from Appendix B

Solution

Oxidation: Fe(s) → Fe2+(aq) + 2e-
Eoox = +0.45 V

Reduction: 2H+(aq) + 2e- → H2(g)
Eored = 0.00 V

Net: Fe(s) + 2H+(aq) → Fe2+(aq) + H2(g)
Eocell = +0.45 V

Since Eocell > 0, the reaction will occur towards the product side spontaneously. If you put iron nail to hydrochloric solution iron nail will start to dissolve immediately.

Literacy

1. EoCa/Ca2+ = +2.76 V
EoFe/Fe2+ = +0.44 V
Can Ca2+ ions oxidize the metallic iron to Fe2+?

Hint: look carefully to signs of standard electrode potentials!

2. What will happen whenzinc plate will be immersed into the solution of silver nitrate? Calculate Eocell forthis reaction.
Answer: +1.56 V

Terminology

- To immerse – батыру / погружать

8.3 ELECTROCHEMICAL CELLS

Why are batteries harmful to the environment when they are thrown in the garbage?

Battery waste container

You will:

- understand that galvanic cell is used to convert energy gained by chemical reaction to electrical one;
- explain how galvanic cell works;
- explain how rechargeable batteries work.

Do you remember the reaction when copper was reduced by zinc? Zinc was oxidized by copper and lost its electrons while copper was gaining those electrons. However wouldn't it be interesting if we could separate these two half-reactions and make electrons travel over a wire? Why would it be interesting to make electrons travel over a wire? Because when electrons travel over wire it makes current and this current can do useful things like powering of a motor, etc. It can be said that we can construct a simple battery by doing so.

So, when oxidation-reduction half-reactions of Zn-Cu are carried in separate containers without bringing the two reactants into direct contact with each other, the flow of electrons occurs through an external pathway. These kinds of devices are called voltaic cells or galvanic cells.

In a zinc-copper chemical cell, a zinc bar is inserted in a solution of ZnSO4 and a copper bar in a solution of CuSO4. The two solutions are connected by an external pathway, which is called a salt bridge - an inverted U-shaped tube containing a solution of a salt such as KNO3 or NaNO3. A porous cotton plug is then placed into the two ends of the U-tube to prevent the two solutions from mixing. The two metal strips are connected by wires that lead to a voltmeter.

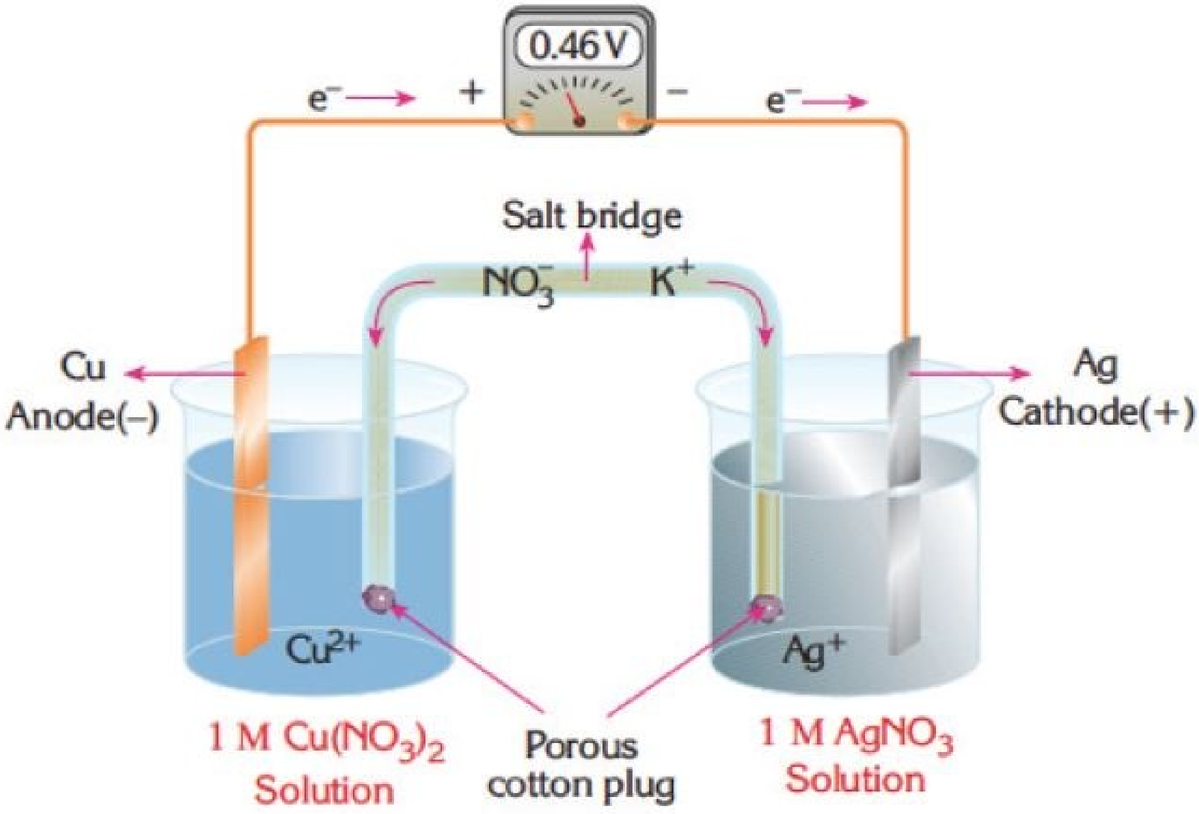
Ok, if our chemical cell is a battery, what is a positive terminal, negative one? Well, the terminal where the electrons are coming is the zinc bar, it is the negative electrode, or as often we call it - anode. The other side, copper bar, is the positive electrode or cathode.

Now, our next question what is a voltage? We can easily answer this question by calculating Eo of cell. Look at Example 1 from the previous topic. Eocell will be +1.10 V.

So, what will happen to zinc and copper bars? Reality is that solid zinc by giving its electrons will become Zn2+ and start to dissolve in a ZnSO4 solution while Cu2+ from a CuSO4 solution will take those electrons and precipitate on the copper bar. Over time wouldn't our solutions become imbalanced? One will become too positive and electrons will not leave the ZnSO4 solution, on the other hand, the CuSO4 solution will become too negative. So what can we do to make sure that it doesn't happen too quickly? Well, that why we use the salt bridge, it keeps solutions from becoming too positive or too negative by exchanging its ions with solutions.

Shorthand notation for galvanic cells

It is a little bit annoying to draw a picture for every galvanic cell when you want to represent it. So, there is a shorthand notation that you use.



Copper-silver chemical cell

Example 1

Write shorthand notation for Zn-Cu galvanic cell

Solution

First, we write information about anode then that of a cathode. Always remember that "A comes before C". Our anode is Zn and cathode is Cu. Solid zinc is oxidized to the zinc ion. We will use a vertical line to show phase boundary. Also, we need to mention molarity of the solution:

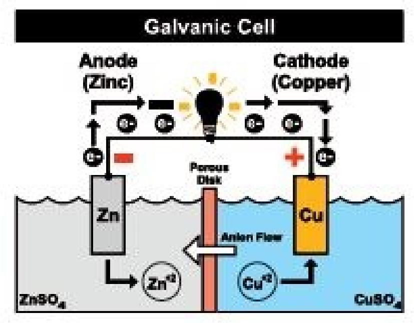
Zn(s) | Zn2+(aq) (1M)

Copper ion is reduced to solid copper:

Cu2+(aq) (1M) | Cu(s)

Finally, we need to write two half-reactions together: Here double vertical line represents the salt bridge.

Zn(s) | Zn2+(aq) (1M) || Cu2+(aq) (1M) | Cu(s)



Zn-Cu chemical cell

Example 2

Write RedOx reaction that occurs on an aluminum-zinc cell. Draw a cell diagram for a voltaic cell in which his reaction takes place. Calculate voltage and write shorthand notation for this cell.

Solution

First of all, we need to write half-reactions that take place in this galvanic cell. Zinc's Eo has got a higher value than that of aluminum therefore, Al is being oxidized. Then it will be easy to calculate voltage of the cell.

Oxidation: Al(s) → Al3+(aq) + 3e- 2

Eoox = +1.66 V

Reduction: Zn2+(aq) + 2e- → Zn(s) 3

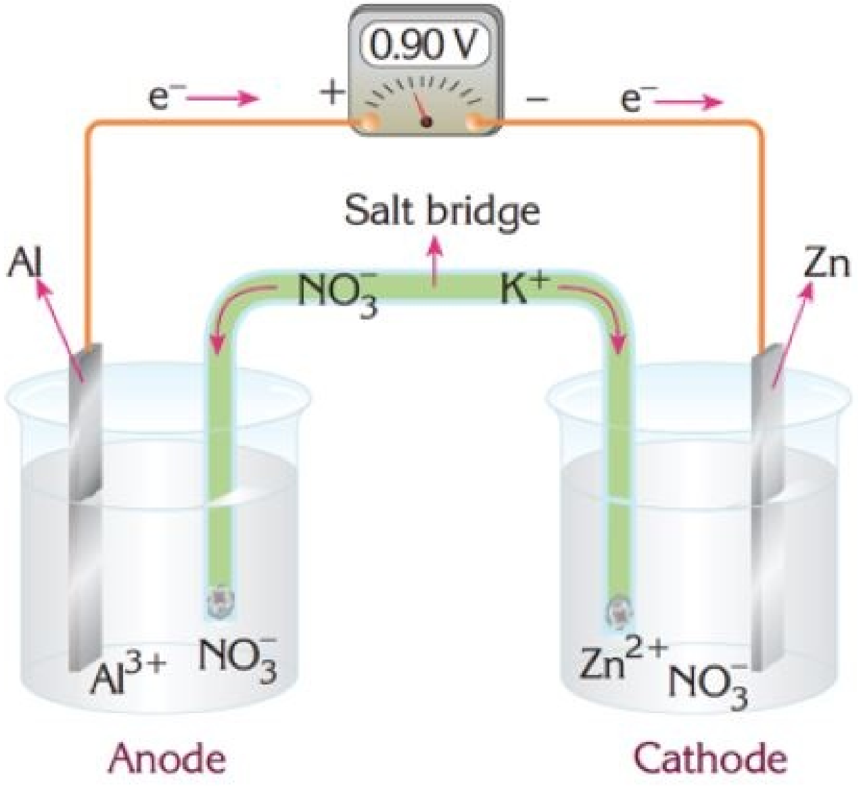
Eored = -0.76 V

Cell: 2Al(s) + 3Zn2+(aq) → 2Al3+(aq) + 3Zn(s)

Eocell = +0.90 V

Diagram:

Shorthand notation: Al(s) | Al3+(aq) Anode || Zn2+(aq) | Zn(s) Cathode



Al-Zn chemical cell

As in any electrochemical cell, there are cathode and anode in a car battery. The cathode is a lead (IV) oxide (PbO_2) while the anode is sponge made up of lead metal (Pb) and the solution is sulfuric acid. Therefore, the car battery is also known as a lead-acid battery. Now let's try to understand "chemistry" of the lead-acid battery.

The following reaction takes place inside the battery:

$Pb(s) + PbO_2(s) \rightarrow PbSO_4(s)$ It will be easier to understand if we balance reaction. Don't forget that our medium is acidic due to the presence of sulfuric acid.

The first thing to do is to assign oxidation states of reactants and products. As you could notice, solid lead has oxidation state as zero but after losing two electrons it will increase its oxidation state to plus two, so this reaction is oxidation. The oxidation state of lead in a lead (IV) oxide is plus four and after reaction lead will decrease its oxidation state to plus two by gaining two electrons, so this one is reduction,

Oxidation: $Pb(s) \rightarrow Pb^{2+}(aq)$

But we need to get lead (II) sulfate as a product:

Oxidation: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Reduction: $PbO_2(s) \rightarrow Pb^{2+}(aq)$

But still we need to get lead (II) sulfate as a product:

Reduction: $PbO_2(s) \rightarrow Pb^{2+}(aq)$

Reduction: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

After adding two half-reactions will get cell reaction:

Cell: $Pb(s) + 2SO_4^{2-}$

(aq) + $4H^+$ + $PbO_2(s) \rightarrow 2PbSO_4(s) + 2H_2O(l)$ By use of a table with standard electrode potentials you will calculate that E^o_{cell} is about +2 volt and it means that our redox reaction is spontaneous. Lead (II) sulfate that is produced from the redox reaction will precipitate on cathode and anode.

To recharge the battery, we need only to reverse the reaction and actually, it happens when a car is running. So, now it is clear why car battery can be used over and over again.

Chemistry around us

How does car battery work?

A car battery is a series of six smaller batteries lined up. The voltage of every battery is about 2 volt that gives 12 volts in total for one car battery (although actual the voltage is 12.6).

Research time

Open in browser Electric jellyfish.

Research how jellyfishes produce electricity.

Literacy

1. Draw a cell diagram for the following reaction.

$Mg(s) + Fe2+(aq) \rightarrow Mg2+(aq) + Fe(s)$.

Write the half-reactions for the anode and cathode. Write shorthand notation for this galvanic cell. Calculate voltage of the cell.

2. Calculate the standard cell potential of a cell constructed with nickel (Ni) and copper (Cu) electrodes. Write shorthand notation for the cell.

8.4 ELECTROLYSIS

Which of the following metals, if coated onto iron, would prevent the corrosion of iron: Mg, Cr, Cu?

You will:

- explain the process of electrolysis;
- suggest products for electrolysis of substances.

In previous topic you learned that galvanic cells can be used to produce electricity. Therefore, galvanic cell - a spontaneous redox reaction is used to produce an electric current. However, can electric current be used to drive a non-spontaneous redox reaction? For example, can we use electric current to reduce zinc by copper? As you would suggest, the answer is yes, we can. Such reactions take place in a cell called - electrolytic cell.

Let's consider redox reaction of Cu-Zn:

Oxidation: Cu(s) → Cu2+(aq) + 2e-

Eoox = -0.34 V

Reduction: Zn2+(aq) + 2e- → Zn(s)

Eored = -0.76 V

Cell: Cu(s) + Zn2+(aq) → Cu2+(aq) + Zn(s)

Eocell = -1.10 V

A negative cell potential means that our reaction is nonspontaneous redox reaction. This reaction needs some help from the outside, so electric current is the "help" that can force our reaction to happen. Now, let's talk about electrodes, in voltaic cells anode is a source of electrons that why it is negative electrode and cathode is a positive electrode. However, in electrolysis process anode is no more source of electrons, now the negative electrode is cathode because electrons are forced on it by a battery. Thus, the signs of the electrodes are opposite for galvanic and electrolytic cells.

Electrolysis of water

Water is electrolyzed in the presence of a small amount of sulfuric acid or sodium sulfate added to water to provide ion flow in a solution. In the process of electrolysis of water, H2 is collected at the cathode and O2 is collected at the anode:

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

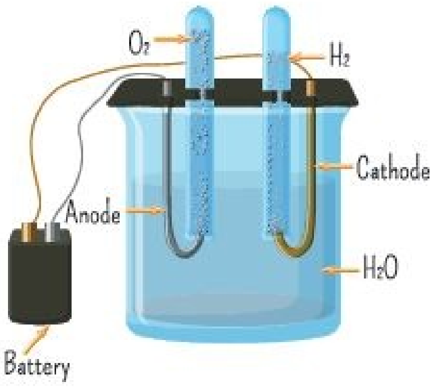
$E^o_{red} = -0.83$ V

Anode: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2e^- + 2H^+(aq)$

$E^o_{ox} = -1.23$ V

Cell: $H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$

$E^o_{cell} = -2.06$ V



Electrolysis of molten NaCl

In the electrolysis of molten NaCl, sodium ions move towards the cathode and chloride ions move towards the anode.

Cathode : $2Na^{+}(aq) + 2e^{-} \rightarrow 2Na(l)$;   Eored = –2.71 V

Anode : $2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-}$; Eoox = –1.36 V

Cell : $2Na^{+}(aq) + 2Cl^{-}(aq) \rightarrow 2Na(l) + Cl_2(g)$; Eocell = –4.07 V

The negative value of the cell potential, Eocell, shows that the system requires an external energy source to occur. That is, the reaction is an electrolysis reaction.

Electrolysis of aqueous solutions

Example 1

Suggest products for electrolysis of aqueous solution of sodium chloride.

Solution

Let's compare standard electrode potentials for oxidation and reduction half reactions of water and molten NaCl:

Oxidation: $2Cl^{-}(aq) \rightarrow Cl_2(g) + 2e^{-}$;   Eoox = –1.36 V

(anode) $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2e^{-} + 2H^{+}(aq)$;   Eoox = -1.23 V

Reduction: $2Na^{+}(aq) + 2e^{-} \rightarrow 2Na(l)$;   Eored = –2.71 V

(cathode) $2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$;   Eored = -0.83 V

After consideration of reactions above we can conclude that it is more easier to reduce water than sodium ions,

Eored(water) > Eored(Na^+).

There is no significant difference between Eo at the anode. So, the cell reaction will be:

Cell : $2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)$;   Eocell = –2.21 V

Thus, products for electrolysis of aqueous solution of sodium chloride are $Cl_2(g)$, $H_2(g)$ and $NaOH(aq)$.

There are some rules that you can use while writing electrolytic equations of water solutions.

The cathode processes.

If the cation of salt is located between Li and Al (inclusive) in the activity series of metals, water molecules will be reduced at the cathode

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

If the cation of salt is located between Mn and Pb (inclusive) in the activity series of metals, both metal ions and water molecules will be reduced at the cathode

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$,

$Me^{n+}(aq) + ne^- \rightarrow Me^0(l)$

If the cation of salt is located after hydrogen in the activity series of metals, only metal ions will be reduced at the cathode

Cathode: $Me^{n+}(aq) + ne^- \rightarrow Me^0(l)$

The anode processes.

All anions can be divided into two groups:

I group - S2-, I-, Br-, Cl-, etc

II group - SO42-, NO3-, PO43-, all other oxyanions, F

If the anion is member of 1st group, then anion itself will be oxidizedon anode

Anode : An-(aq) → A0 + ne-

If the anion is member of 2nd group, water molecules will be oxidized on anode

Anode: H2O(l) → ½ O2(g) + 2e- + 2H+(aq)

Example 2

Suggest products for electrolysis of silver nitrate solution

Solution

At the cathode silver Ag will be reduced while water molecules will be oxidized at the anode according to the rules above.

Cathode : 2Ag+(aq) + 2e- → 2Ag(l);   Eored = -0.80 V

Anode: H2O(l) → ½ O2(g) + 2e- + 2H+(aq);   Eoox = -1.23 V

Cell : 2Ag+(aq) + H2O(l) → 2Ag(l) + ½O2(g) + 2H+;   Eocell = –2.03 V

$2AgNO_3(aq) + H_2O(l) \rightarrow 2Ag(l) + \frac{1}{2}O_2(g) + 2HNO_3(aq)$

Application of electrolysis

Purification of copper

Copper used in electrical wires and circuits should be very pure. So, electrolysis is used to refine crude copper. Impure copper is given a positive charge (anode), and pure copper is given a negative charge (cathode). As the purification proceeds, the impure copper in the anode is forced into a solution by the electric current.

Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

The Cu^{2+} ions in the solution migrate to the cathode, where they are more easily reduced than water.

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

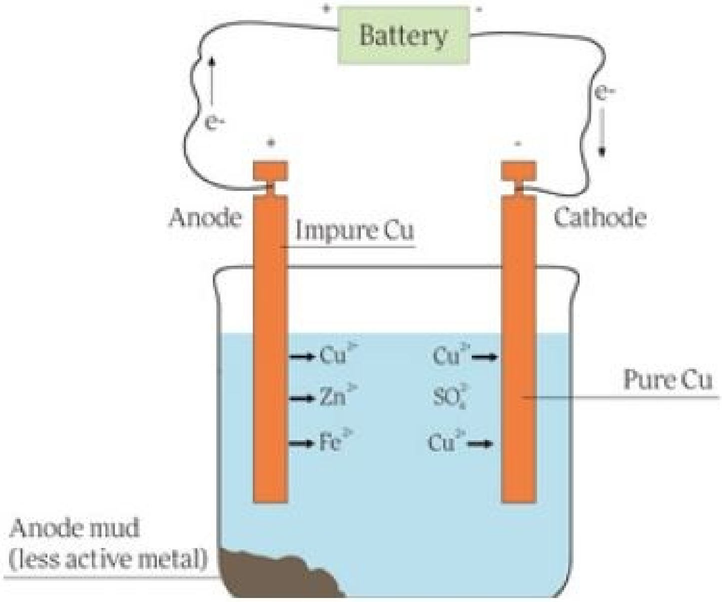
Hence, pure copper plates out on the cathode.

Plating of metals

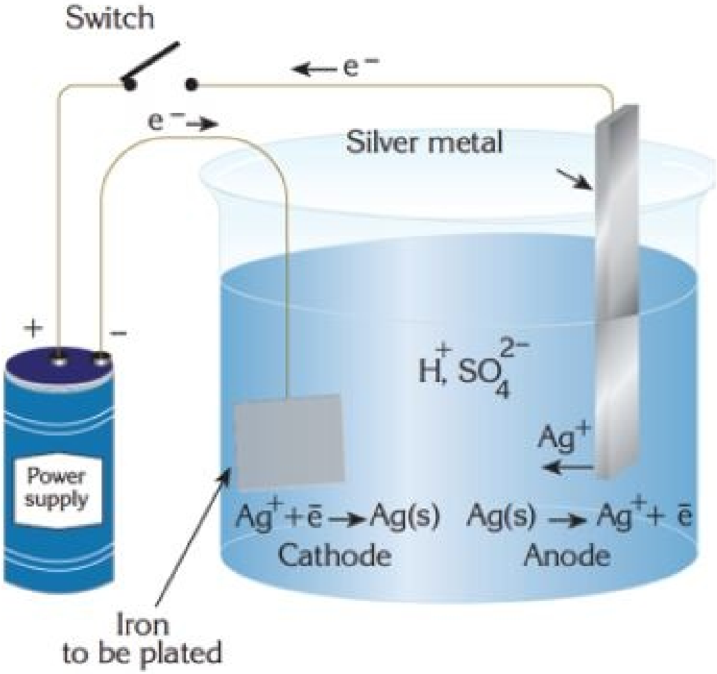
The process of electroplating metals is another important application of electrolysis. Metals that easily corrode (Fe and Cu) can be plated by metals that are resistant to corrosion. Chromo-plating steel parts used in vehicles is a good example of electroplating. Steel bumpers become more corrosion-resistant when they are electroplated with nickel first, then with chromium.

Silver can be used to plate copper or brass to produce electrical connectors, since silver is stained much more slowly and has a higher conductivity than the other metals. The benefit of using silver is decreasing the surface electrical resistance, which results in a more efficient electrical connection.

Low force/low voltage separable connectors used in computers, and other electronic devices, are typically plated with gold or palladium over a barrier layer of nickel. The tail ends of these connectors, which are usually joined to the device by soldering, are plated with a tin-lead alloy, or pure tin.



Purification of copper with electricity



Plating of iron with silver

Quantitative aspect of electrolysis

There is a simple relationship between the amount of electricity that passes through the electrolytic cell and the amount of a substance undergoing a chemical change. This is known as Faraday's Law of electrolysis.

The formula for calculations:

$$n(e) = \frac{I \times t}{F} \quad \text{or} \quad m = \frac{M \times I \times t}{F \times q}$$

where n - mole number

M - molar mass/atomic mass

I - current, unit is ampere

t - time, unit is seconds

F - Faraday's constant, it is equal to F = 96485 Coulombs

q - is a charge of an ion

Example 3

Calculate the mass of copper produced by the reduction of Cu2+ ions at the cathode, using a current of 1.2 amperes for 30 minutes.

Solution

Balanced equation of the reduction reaction of Cu2+ is

$Cu2+(aq) + 2e- \rightarrow Cu0(s)$

We can use the formula, don't forget to convert time from min to sec:

$$m(Cu) = \frac{63.5 \times 1.2 \times 1800}{96485 \times 2} = 0.710\ g$$

Activity

Choose one of the electrolysis factories from our country and write about it:

- - give the informations about company
- - about production metals.

Research time

Open in browser Electrolytic Refining.

Research how are metals purified by electrolytic method.

Chemfact

In 1807-1808 British chemist Humphry Davy discovered six chemical elements, such as K, Na, Mg, B, Ca, Ba. These metals isolated by electrolysis from salt minerals.

Chemistry around us

The main location of copper deposits are in Shygys Konyrat and Zhezkazgan. In Balkhash city copper is extracted from minerals by electrolysis (hydrometallurgy and electrometallurgy). The extraction of copper from the mineral requires a large amount of electrical energy.

Literacy

1. Why was iron discovered much more later than copper?

2. Why was alkali metals discovered much later than copper and gold?

3. Suggest products for the electrolysis of CuSO4 solution, what are the anode and cathode half-reactions?

4. In industry, aluminium is produced from the electrolysis of Al2O3 at 100°C.

$$2Al2O3 \rightarrow 4Al + 3O2$$

What is the electrical charge required to produce 4.15 kg of aluminum metal?

5. Suggest which salt will be 1st to be electrolysed from a mixture of molten NaI, MgCl2 and CuBr2 salts.

6. A constant current of 16 A was passed through molten aluminum oxide for 3 hours. Calculate the mass of produced aluminum.

QUESTIONS AND PROBLEMS

1. What is the oxidation number of sulfur in

- - H2SO4
- - H2S
- - SO2
- - FeS2?

2. What is the oxidation number of chlorine in

- - HClO4
- - HCl
- - Cl2O7
- - KClO3?

3. What is the oxidation number of manganese in

- - MnF4
- - Mn2O7
- - MnO(OH)
- - HMnO4 ?

4. What is the oxidation number of nitrogen in

- - N2H4
- - NH4Br
- - N2H5Cl
- - HNO2?

5. Calculate the oxidation state of the element indicated in each of the following problems:

- - What is the oxidation state of hydrogen in NaH?
- - What is the oxidation state of iron in Fe2O3?
- - What is the oxidation state of boron in Na3BO3?
- - What is the oxidation state of bromine in HBrO3?
- - What is the oxidation state of chromium in K2CrO4?
- - What is the oxidation state of oxygen in BaO2?

6. Nitrogen dioxide is prepared by reacting copper with concentrated nitric acid. What should the values of a, b, x and y be in order to balance the following equation?

aCu + bHNO3 → xCu(NO3)2+ yH2O + 2NO2

7. Determine a, b, c numbers in the following equations:

- - CaHb + cO2 → 4CO2 + 4H2O
- - aCr + bKNO3 → Cr2O3 + bKNO2

8. Determine unknown compounds:

- - 10HNO3 + 4Zn → NH4(NO3)2 + 3H2O + 4X
- - 8HNO3 + 3Cu → 3Cu(NO3)2 + 4H2O + 2X
- - 2K2CrO4 + 2H2O + 3H2S → 2Cr(OH)3 + 3X + 4KOH
- - I2 + 5NaClO + 2NaOH → 5X + 2NaIO3 + H2O

9. Balance the following oxidation-reduction reaction:

- - Mg + NO3- → Mg2+ + N2O

- - Cu + NO3- → Cu2+ + NO2
- - S + NO3- → SO42- + NO2

10. In the following example, MnO2 and HCl react to form chlorine gas, manganese (IV) oxide and water:

MnO2 + HCl → Cl2 + MnCl2 + H2O

What are the oxidizing and reducing agents?

11. In the following example, PtF6 and H2 react to form Pt metal and HF:

PtF6 + 3H2 → Pt + 6HF

What are the oxidizing and reducing agents?

12. Indicate whether each of the following is an oxidation-reduction reaction or not:

- - H2O + K → KOH + H2
- - Al + FeSO4 → Al2(SO4)3 + Fe
- - KMnO4 → K2MnO4 + MnO2 + O2
- - K2Se + HNO3 → K2SeO4 + NO2 + H2O
- - Br2 + NaOH → NaBr + NaBrO3 + H2O
- - F2 + NH3 → N2+ NH4F

13. Use the half-reaction method to balance the below equations for a reaction in an acidic medium:

- - MnO4- + SO32- → Mn2+ + SO42-
- - MnO4- + NO2- → Mn2+ + NO3-
- - Cr2O72- + I- → Cr3+ + I2-

- - Cr2O72- + NO2- → Cr3+ + NO3-

14. Use the half-reaction method to balance the following equations in a basic medium:

- - CrO2- + ClO- → CrO42- + Cl-
- - MnO4- + I- → MnO42- + IO4-
- - NO3- + MnO2 → MnO42- + NO2-
- - I- + Cl2 → IO3- + Cl-

9 CHAPTER

ANALYTICAL METHODS

CHAPTER 9: ANALYTICAL METHODS

9.1 ANALYTICAL METHODS IN MODERN RESEARCH

How do scientists weigh molecules - the smallest particles of matter that cannot be seen or touched?

You will:

- know the application areas of instrumental methods of analysis;

Modern methods of research in chemistry

To understand what is an analytical method and why do we need it, it is important to define the analytical chemistry itself. Simply, analytical chemistry can be described as the science of determining the chemical composition of compounds and their chemical structure. An analytical method is a set of techniques for determination of qualitative, quantitative, structural composition of substances.

Analytical methods are constantly alters, new approaches are taken, new principles are used. In the 9th grade you were introduced to simple qualitative analytical methods of determining presence of specific ions in substances. These methods can be classified as classical methods of analysis.

However, there is another type of methods - instrumental methods of analysis or physico-chemical methods. In general, instrumental methods are fast, accurate and sensitive. The sensitivity of these methods allows performing analytical operations with quantities of substances hundred times smaller than in the classical methods. The chromatography, mass spectrometry, nuclear magnetic resonance and X-ray structural analysis are some examples of instrumental methods.

Chromatography

The chromatography is a very important method, serving not only for analytical purposes but also for the separation of substances which are very similar in chemical properties. The latest chromatographic methods can be used to analyze gaseous, liquid and solid substances.

Chromatography provided information on the structure and properties of many classes of organic compounds. The application of chromatographic methods for the separation of proteins had a huge impact on the development of modern biochemistry. Chromatography is successfully used for research purposes in various fields: for monitoring illegal drug use, identifying antibiotics, analyzing various classes of pesticides, monitoring the environment and obtaining data on the composition of the atmospheres of the planets in the solar system. More than ten works (between 1957-1980) performed with the use of chromatographic methods, were awarded the Nobel Prize, which indicates the importance of chromatography as a method of analysis.

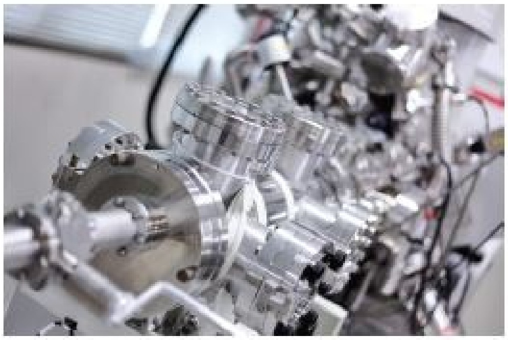
Study of chromatography is used to separate components of a plant

Mass spectrometry

Mass spectrometry has been used to determine the isotopic composition of elements and measure their atomic masses, in XX century mass spectrometry led to the discovery of stable isotopes. The age of rocks, geological and archaeological objects is determined by use of mass spectrometry. The neutral and ionic composition of the upper atmosphere of the Earth, Mars and Venus was measured with the help of mass spectrometry. The most important application of mass spectrometry is to identify the structure of organic compounds. Molecular analysis of complex mixtures of organic compounds can be carried out only after chromatographic separation.

NMR spectroscopy

NMR spectroscopy found its application as method for studying structure of substances in chemistry and biology. NMR allows to determine the spatial structure of the molecule, e.g., protein structure. In chemistry and pharmacology, NMR spectroscopy is an important method for establishing the correct structure of synthesized drugs. The NMR phenomenon has also found its application in medicine in the form of magnetic resonance imaging (MRI), as a visualization method for clinical diagnosis. One of the main areas of application of MRI are diagnosis of cancer and the detection of tumors.



X-ray photoelectron spectrometer. X-ray structural analysis methods study the geometry of molecules.

Ultraviolet–visible spectrometer

Chemfact

There are bacteria in oil wells which convert methane in an energy source. Chemists were interested in the conversion process. Then, in 1979 it was found that the bacteria use a coenzyme, given the trivial name ‘methoxatin’ which oxidizes methane to methanol. Methoxatin was a new compound with an unknown structure and it proved exceptionally difficult to solve the structure by NMR. However, methoxatin was found by X-ray crystallography to be a polycyclic tricarboxylic acid.

Chemfact

Scottish chemist William Ramsay discovered noble gases. He used metallic magnesium to eliminate the oxygen and nitrogen chemically. He performed a spectroscopic analysis of the non-consumed gas and discovered in its spectrum the rays of an unknown element. He called this element argon, meaning "inert".

Chemistry around us

Magnetic resonance imaging (MRI) is a method of obtaining tomographic medical images of internal organs and tissues.

Literacy

1. What is analytical chemistry?

2. What is the difference between classical and instrumental methods of analytical chemistry?

3. What is the main purpose of using mass spectrometry?

Terminology

- magnetic resonance spectroscopy - магниттік-резонансты спектроскопия / магнитно-резонансная спектроскопия

9.2 CHROMATOGRAPHY

What is the basic physical principle on which chromatography can be used to separate mixtures?

You will:

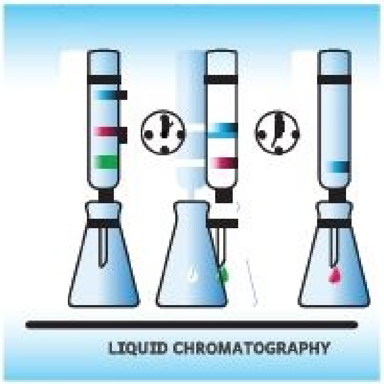
- describe the principles of separation of substances by paper chromatography and calculate the retention factor for the released component.

To separate all possible mixtures, chromatography is very often used for analyzing and isolating individual substances from the mixtures in laboratories: this is one of the best methods for separation and analysis of mixtures.

Chromatography is a method for separating and identifying the components of the mixture.

Chromatography is also used in industry when it is necessary to purify and separate similar substances - organic and inorganic, from lanthanides to amino acids. Its essence is that the individual components of the mixture (liquid or gas) are kept in different ways by an adsorbent material that is able to absorb certain chemical compounds selectively. The word "chromatography" means: "chromo" - color, "grapho" - write. In the 20th century, scientists discovered the meaning of green coloring of plants. It turns out that plants absorbed light and absorbed energy is used to synthesize nutrients! It was necessary to isolate and purify the pigments of the green leaf - chlorophyll. And they are so close in properties that they could not be divided.

Modern gas and liquid chromatographs are complex devices with automatic control, often with a microcomputer, which schedules the research and produces ready-made results. Of course, this is not available for a home laboratory or a mug. However, this method of analysis began with simple tricks that are available to a beginner chemist.



Column chromatography

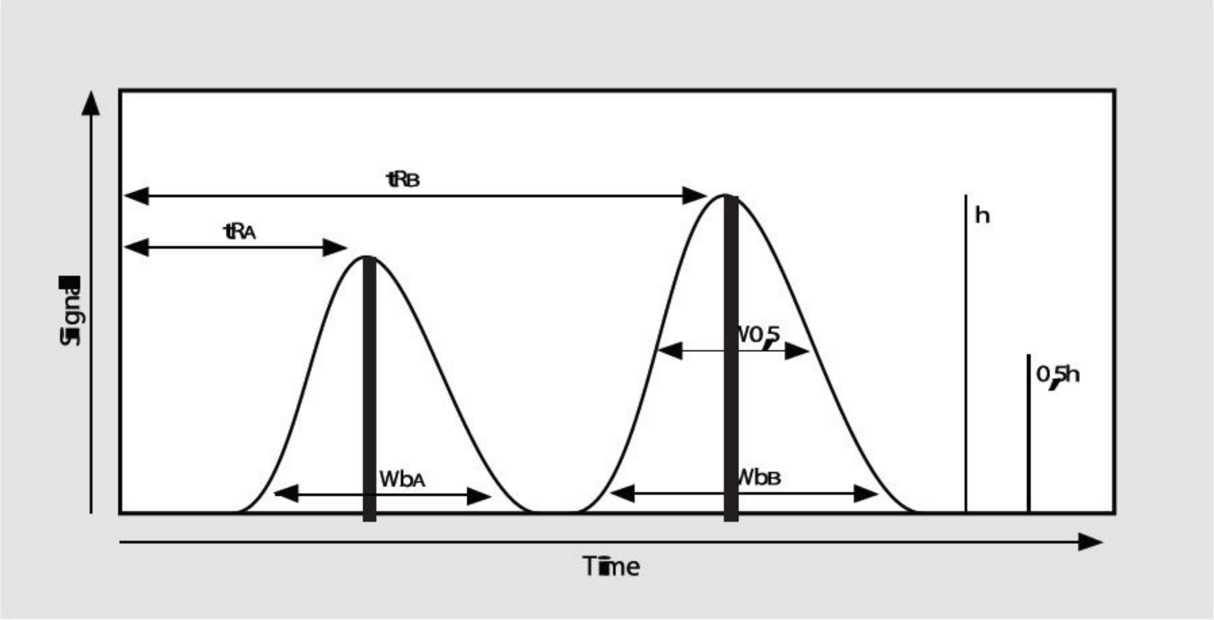
Gas chromatography

Paper chromatography

Paper chromatography - a method of separation and analysis of mixtures of substances, based on their distribution between the mobile and stationary liquid phases; as a carrier of a stationary liquid phase, a paper is used.

In paper chromatography, special types of paper are used, differing in numbers, with increasing the density of paper. Paper retains in the pores water, which is a stationary liquid phase. The sample solution is applied as a droplet on a sheet of paper at some distance from the edge. After evaporation of the solvent, the edge of the sheet is placed in a sealed chamber containing the developer-a mobile liquid phase (for example, alcohols, ketones, phenols, carbon tetrachloride, chloroform and other mixtures thereof, and mixtures with inorganic solvents). In this case, the initial spot moves along the developer's current and the mixture are divided into components. If the substances are not colored, then the chromatogram is shown, for example, by spraying with an indicator solution, viewed in ultraviolet rays, etc. The ratio of the distance Rf (retention factor) traversed by the spot to the distance traveled by the developer front m under the same experimental conditions is a constant value; Rf for different substances differ in value and can be used to identify compounds.

Rf = (distance traveled by solute)/(distance traveled by solvent)



A chromatography graph with measurements and symbols.

Quantitative determinations of various substances in the spots of the chromatogram are carried out by usual analytical methods. There are one-dimensional, two-dimensional, circular, column and electrophoretic chromatograms.

Types of chromatography:

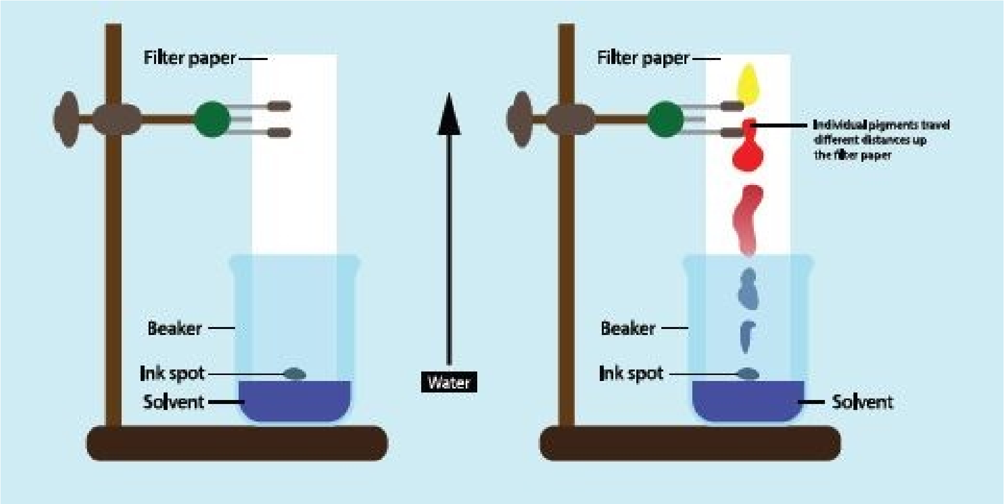
- - Thin layer chromatography
- - Paper chromatography
- - Gas-liquid chromatography
- - Gel chromatography
- - Column chromatography and etc.

Laboratory work

Paper chromatography

Chemists-analysts use special chromatographic paper, but for our experiments, the usual filter paper, or even a blotter, will do. Take a square sheet of paper and in the middle drip the test solution containing a mixture of colored substances. This can be an alcohol tincture of medicine, such as valerian or calendula, or a chlorophyll extract you have prepared, or a mixture of dyes, made up specifically for this experiment. A stain forms on the paper. At the center of it, drip a few drops of the solvent: in the above examples, alcohol should serve as the solvent, and you can not replace it with cologne - it contains substances that can distort the course of the experiment.

So, you have dropped a few drops of the solvent, and it, as if on a wick, moving between the paper fibers, carries the colored substances from the stain in all directions. Depending on the nature of the substance and its molecular weight, the experiment is faster or slower, but sooner or later, several rings of different colors appear on the sheet. How many rings - depends on how many substances were in the mixture being analyzed.



Chemistry around us

Paper chromatography is used to separate and analyze inorganic and organic substances in natural and industrial materials (for example, resins in petroleum products, rare earth elements in rocks and minerals).

Chemfact

Russian botanist Mikhail Semyonovich Tsvet developed chromatographic analysis methods, and he showed that there exist two types of chlorophyll called chlorophyll a and chlorophyll b.

Literacy

1. What is a Rf value in chromatography?

2. How is chromatography used in real life?

3. What are some types of chromatography?

4. How does chromatography work?

5. How do you extract chlorophyll from plants?

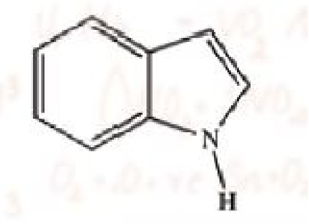
Terminology

- chromatography - хроматография /хроматография
- essence - мағынасы, мәні /сущность
- schedules - графиктер /графики
- retention factor - ұсталу коэффициенті /коэффициент удержания
- cologne - әтір / одеколон

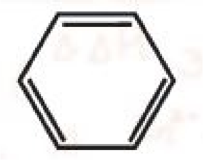
QUESTIONS AND PROBLEMS

1. Cyclopentene, C5H8, can be represented as:

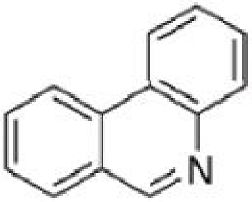
Use this information to calculate the relative molecular mass of the compound shown below:

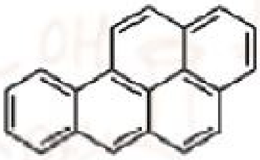


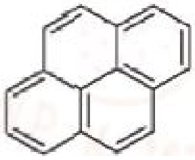
2. Benzene, C6H6, can be represented as:



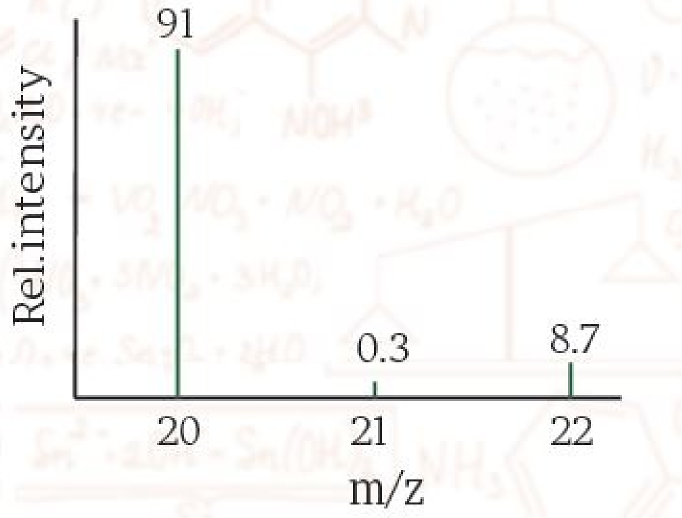
Use this information to calculate the relative molecular masses of the compounds shown below:



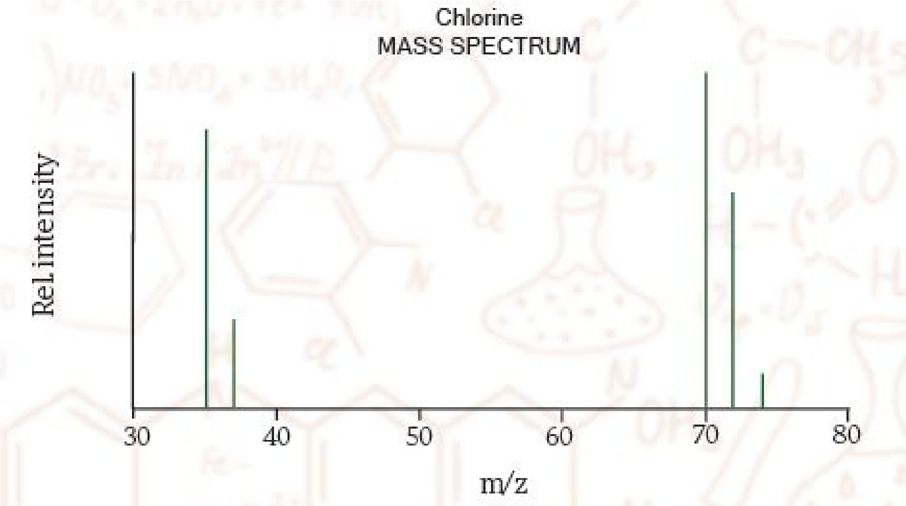




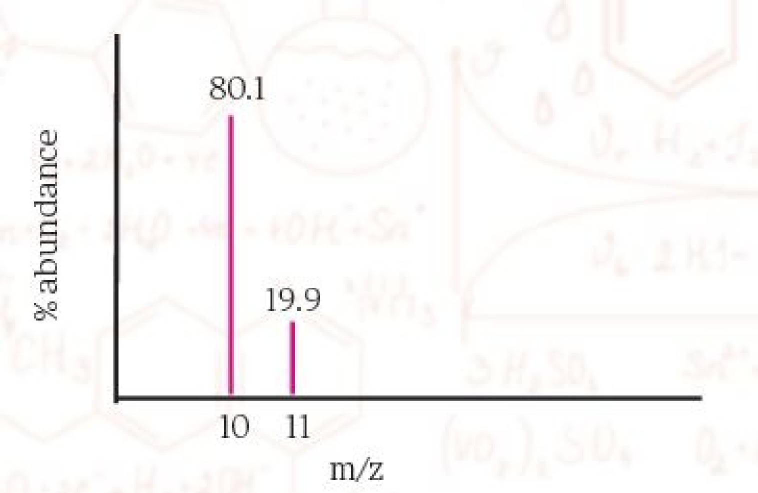
3. Use figure to estimate the atomic mass of the element neon.



4. Use figure to estimate the atomic mass of the chlorine.



5. Find atomic mass and symbol of unknown chemical element.



10 CHAPTER

HALOGENS

CHAPTER 10: HALOGENS

10.1 HALOGENS AND THEIR PROPERTIES

Why hydrogen is accepted as both a halogen and an alkali metal?

You will:

- explain the patterns of changes in the physical properties of halogens in the group 17.

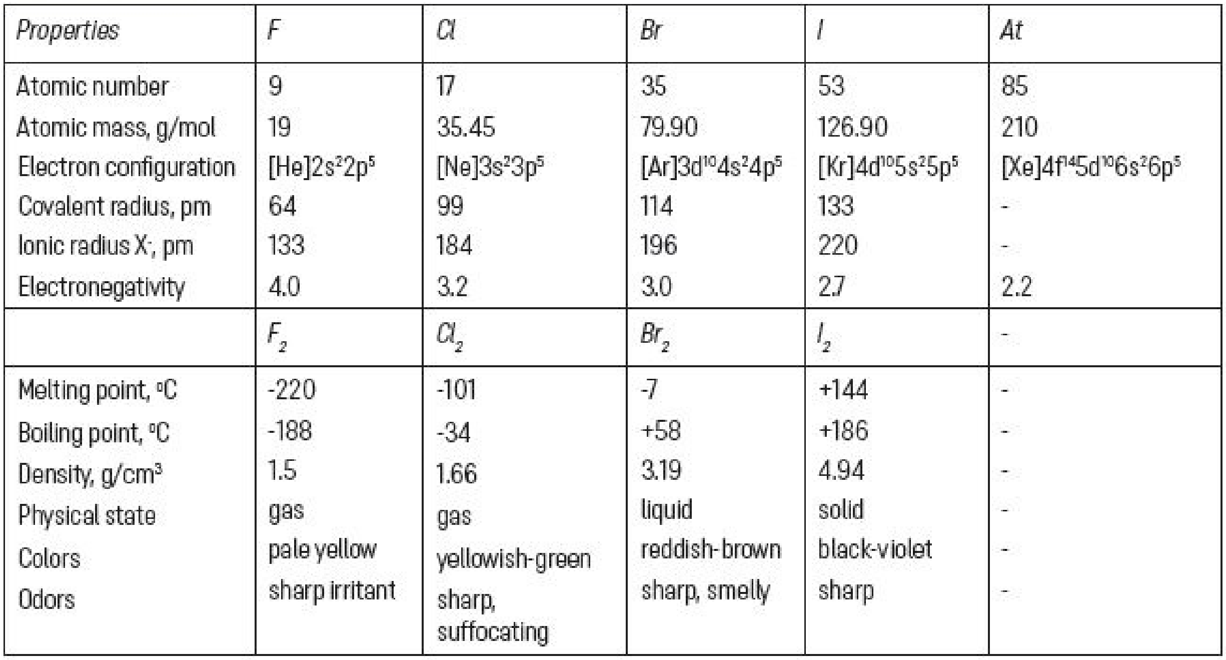
Group 17 elements fluorine, chlorine, bromine, iodine and astatine are named as halogens. (from Greek “halo” means “salt” and “genes” means “born”, so that halogens stands for salt producers). Halogens are considered to be the highest reactive nonmetals. They exist in diatomic form when they are in their elemental form. Astatine is a radioactive element, with the most stable isotope having half life of 8.1 hours.

Occurrence

The abundance of halogens decrease as we go down the group. Fluorine generally occurs as insoluble fluorides. The common minerals are fluorspar CaF2, cryolite Na3AlF6, and fluoroapatite 3Ca3(PO4)2·CaF2. Fluorine also occurs in small quantities in river plants, bones and teeth of animals. Sea water contains 2.5% of sodium chloride by mass, but chlorides, bromides and iodides of potassium, magnesium and calcium are also present.

The important atomic and physical properties of 17th group elements along with their electronic configurations are given in table.

Table 14 *Physical properties of Halogens*



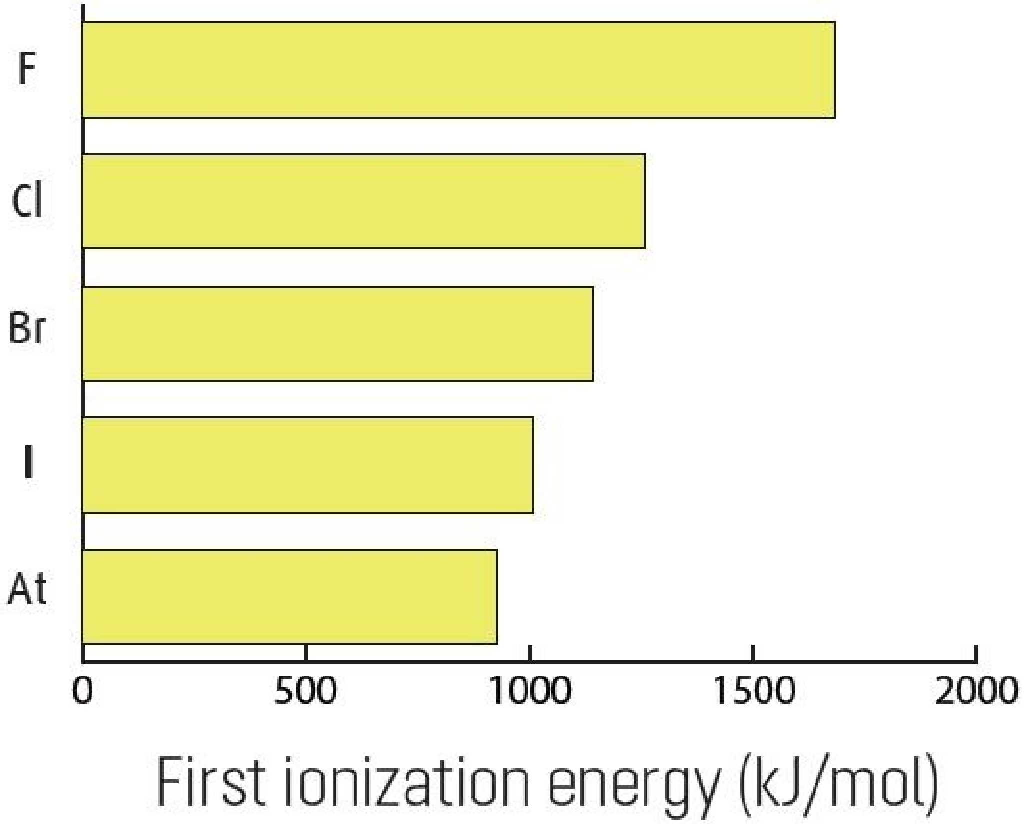
Properties	*F*	*Cl*	*Br*	*I*	*At*
Atomic number	9	17	35	53	85
Atomic mass, g/mol	19	35.45	79.90	126.90	210
Electron configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
Covalent radius, pm	64	99	114	133	-
Ionic radius X^-, pm	133	184	196	220	-
Electronegativity	4.0	3.2	3.0	2.7	2.2
	F_2	Cl_2	Br_2	I_2	-
Melting point, °C	-220	-101	-7	+144	-
Boiling point, °C	-188	-34	+58	+186	-
Density, g/cm^3	1.5	1.66	3.19	4.94	-
Physical state	gas	gas	liquid	solid	-
Colors	pale yellow	yellowish-green	reddish-brown	black-violet	-
Odors	sharp irritant	sharp, suffocating	sharp, smelly	sharp	-

Electron configuration

All of the halogens have 7 valence electrons. They need 1 moreelectron in order to have noble gas electron configuration.

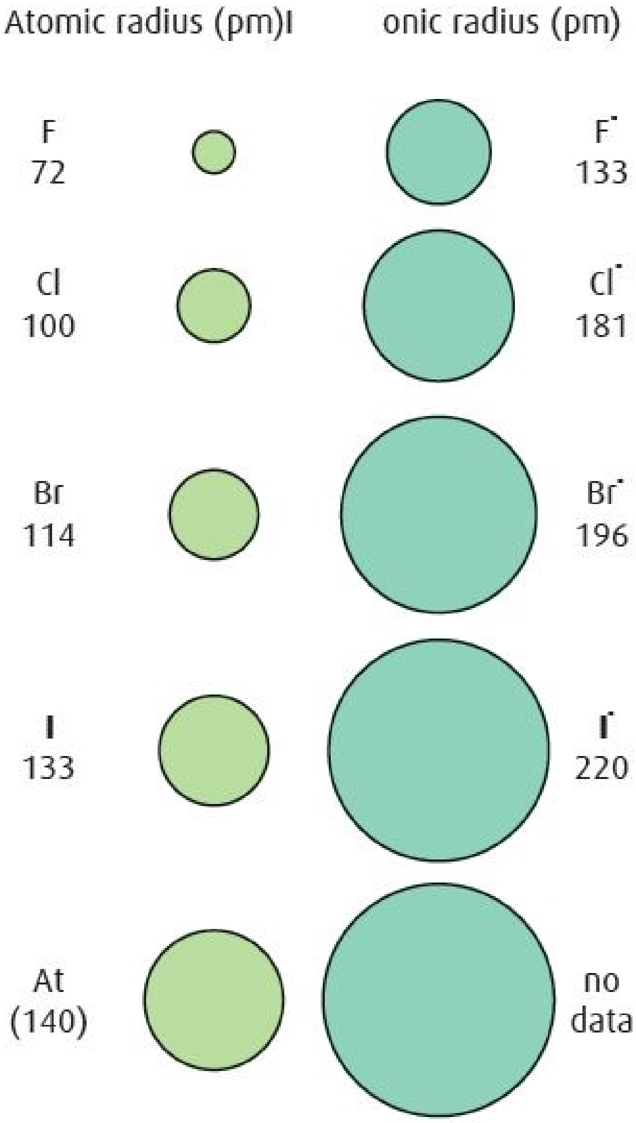
Ionization energy

Halogens have high ionization energy. Due to increase in atomic size, ionization energy decreases down the group.



Atomic and Ionic radii

Atomic radii of halogens increase from top to bottom in the group, hence the pull of the nucleus is shielded by increasing layers of electrons. Fluorine has the smallest radius whether astatine is the biggest.



Electron gain enthalpy

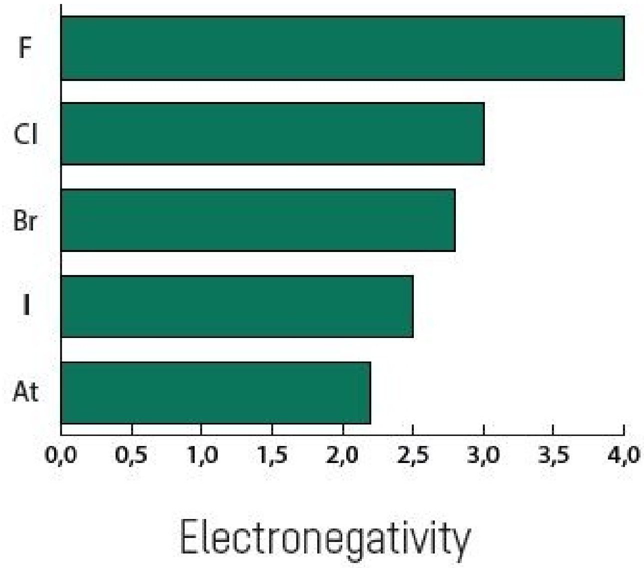
Electron gain enthalpy of the halogens becomes less negative down the group. However, negative electron gain enthalpy of chlorine is bigger than that of fluorine. It is due to small size of fluorine atom.

Table 15 *Electron gain enthalpies of halogens*

Electron gain enthalpy	*kJ/mol*
F	-333
Cl	-348
Br	-324
I	-295
At	-270.1

Electronegativity

Halogens have high electronegativity. The electronegativity of them decreases down the group. Fluorine is the most electronegative element in the periodic table.

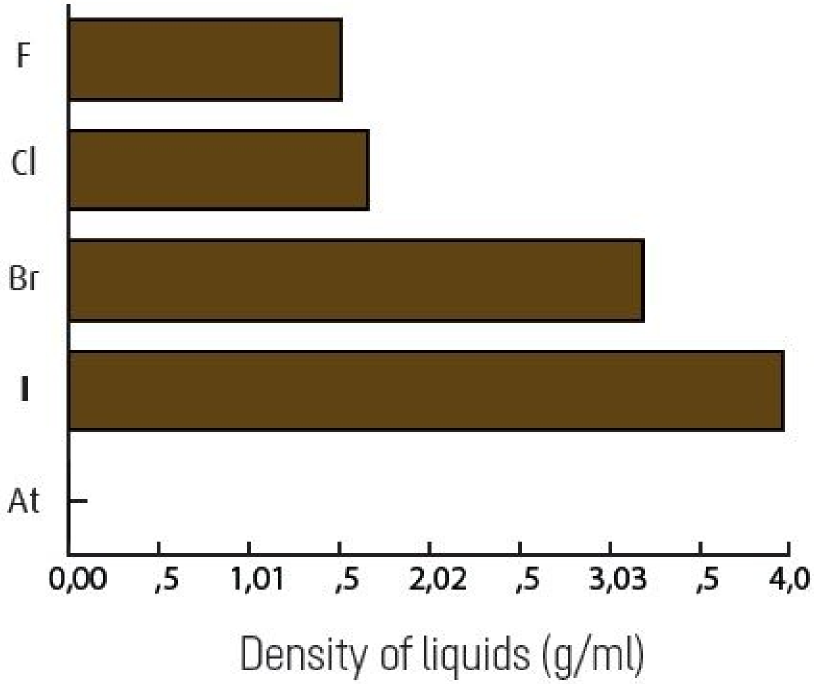


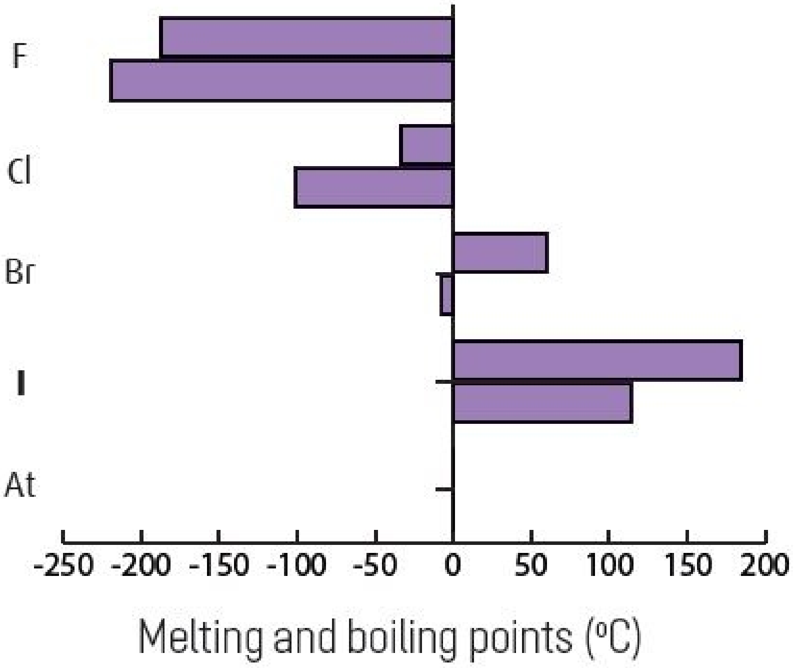
Physical Properties

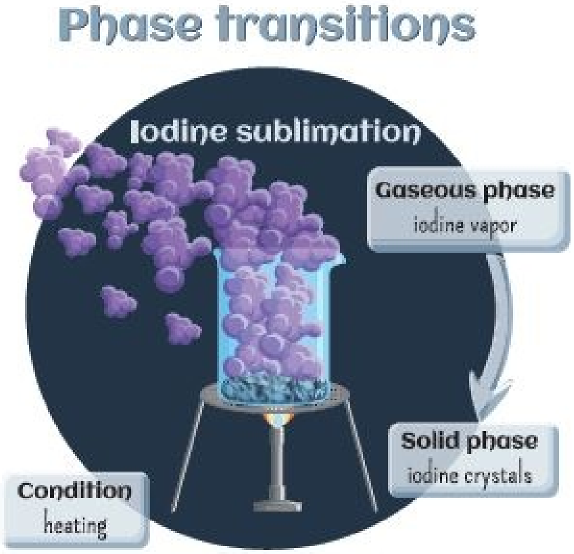
Fluorine is a light-yellow gas with a strong odor. It's poisonous. Chlorine is a gas of yellowish-green color, as well as chlorine has a sharp odor and strongly poisonous. At high pressure and room temperature, it easily passes into the liquid state. Bromine is a reddish-brown liquid with a characteristic unpleasant sharp odor.

Liquid bromine, as well as its vapors are highly poisonous. Bromine is poorly soluble in water and good in non-polar solvents. Iodine is a dark gray solid with a metallic shine. Iodine vapor has a violet color. Iodine easily sublimes, i.e. goes into a gaseous state from a solid, while bypassing the liquid state.

Inhalation of even small amounts of halogens causes severe irritation of the respiratory tract and inflammation of the mucous membrane of the throat and nose. More significant amounts of halogens can cause severe poisoning of the body.




F
Cl
Br
I
At
-250
-200
-150
-100
-50
0
50
100
150
200
Melting and boiling points (°C)


Phase transitions
Iodine sublimation
Gaseous phase
iodine vapor
Solid phase
iodine crystals
Condition
heating

Bromine in a round bottom flask

Chlorine gas in a round bottom flask

Wakame seaweed contains bromine

Literacy

1. What are the physical properties of halogens?

2. Which elements are found in the group 17?

3. What are the physical states of group group 17 elements?

4. Why are halogens found in different states at room temperature?

5. Where is fluorine found in the Earth crust?

6. In 1811 B.Courtois was first observed new chemical element by treating the ash of seaweed with concentrated sulfuric acid. Which chemical element discovered B.Courtois?

Chemistry around us

Iodine compounds, for example Nessler's reagent $KHgI_3$ used for detection of NH_3, and Mayer's reagent Cu_2HgI_4 for determining alkaloids (natural amines) in analytical chemistry.

Wild-growing poisonous herb Hyoscyamus contains alkaloids

Chemistry around us

Bromine compounds are used as fire retardants, especially for fibers, carpets, rags and plastics. Other uses of bromoorganic compounds include high-density drilling fluids, dyestuffs and pharmaceuticals.

Terminology

- to treat - емдеу / лечить;
- corresponding - сәйкес келетін / соответствующий;
- repulsion - тебісу /отталкивание;

- smooth - тегіс / гладкий,плавный;
- steadily - тұрақты түрде /неуклонно;
- excitation - қозу /возбуждение.

10.2 CHEMICAL PROPERTIES AND PREPARATION OF HALOGENS

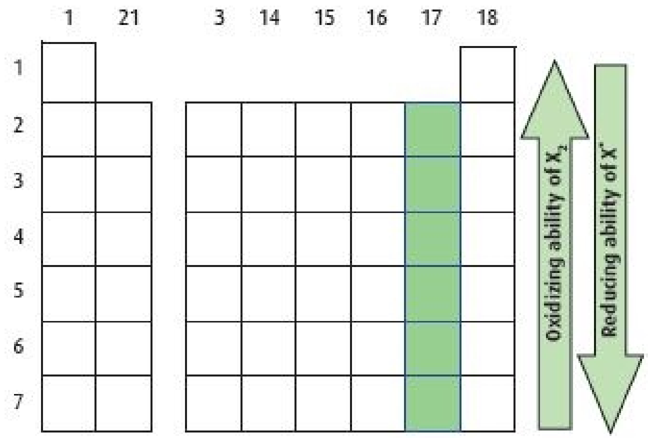
Why iodine does not exist in liquid state at room temperature?

You will:

- know chemical properties of halogens;
- write the redox reactions of halogens.

Chemical properties

All the halogens exhibit –1 oxidation state. However, chlorine, bromine and iodine exhibit +1, +3, +5 and +7 oxidation states. All the halogens are highly reactive. They react with metals and nonmetals to form halides. The reactivity of the halogens decreases down the group. Fluorine unlike other halogens has unusual properties. For example, ionic and covalent radii, melting and boiling points of it are lower than expected. The electronegativity and electrode potentials, oppositely, are higher than expected from the trends which are set by other halogens. This is because of small size of fluorine atom and highest electronegativity.



Changing oxidizing and reducing abilities of elements by group

1. Reactions with nonmetals

Fluorine oxidizes all elements except He, Ne and Ar. It is an extremely reactive element. For example, it reacts with hydrogen explosively, even at –250°C.

$$\mathrm{F2(g) + H2(g) \rightarrow 2HF(g)}$$

$$\mathrm{3F2(g) + N2(g) \rightarrow 2NF3(g)}$$

$$\mathrm{F2(g) + O2(g) \rightarrow O2F2(g)}$$

$$\mathrm{3F2(g) + S(s) \rightarrow SF6(g)}$$

$$\mathrm{Cl2(g) + H2(g) \rightarrow 2HCl(g)}$$

$$\mathrm{3Cl2(g) + 2P(s) \rightarrow 2PCl3(l)}$$

$$\mathrm{Br2(g) + Cl2(g) \rightarrow 2BrCl(g)}$$

$$\mathrm{I2(s) + 5F2(g) \rightarrow 2IF5(l)}$$

2. Reactions with metals

$$3F_2(g) + 2Sb(s) \rightarrow 2SbF_3(s)$$

$$3Cl_2(g) + 2Fe(s) \rightarrow 2FeCl_3(s)$$

$$Br_2(l) + 2Li(s) \rightarrow 2LiBr(s)$$

$$W(s) + 3F_2(g) \rightarrow WF_6(g)$$

$$3I_2(s) + 2Al(s) \rightarrow 2AlI_3(s)$$

Thus, when the aluminum atoms on the left of the equation are oxidized, they lose electrons and become Al^{3+} ions. Another feature of the equation is that the iodine atoms, bound together on the left-hand side as diatomic molecules, take on electron and form I^- ions. Thus, whereas the aluminum atoms lose electrons, the iodine atoms gain them.

3. Reactions with water and oxygen

Fluorine oxidizes water with oxygen, chlorine and bromine react with water to form corresponding hydrohalic and hypohalous acids.

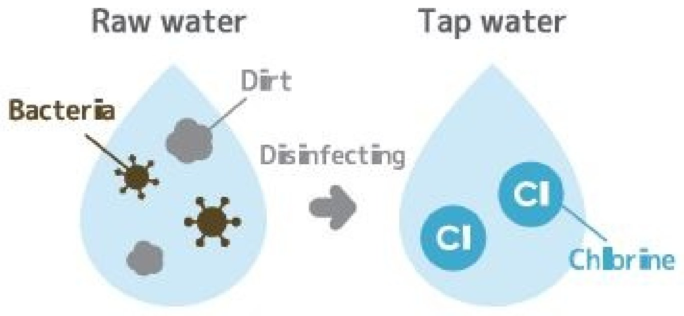
$$2F_2(g) + 2H_2O(l) \rightarrow 4HF(g) + O_2(g)$$

$$Cl_2(g) + nH_2O(l) \rightarrow Cl_2 \bullet nH_2O(aq)$$

$$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$$

The reaction of iodine with water is nonspontaneous.

$$I_2(s) + H_2O(l) \rightarrow HI(aq) + HIO(aq)$$



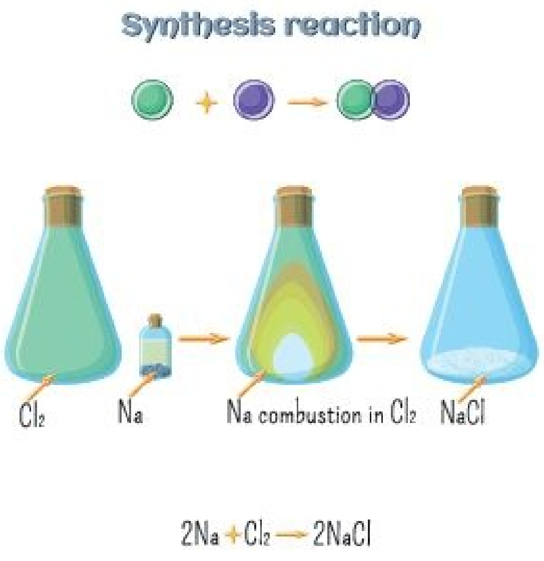
Raw water is disinfected with chlorine

4. Halogens can displace any of the halogens from their salts and acid solutions.

$$\mathrm{F2(g) + 2NaCl(aq) \rightarrow 2NaF(aq) + Cl2(g)}$$

$$\mathrm{Cl2(g) + 2NaBr(aq) \rightarrow 2NaCl(aq) + Br2(l)}$$

$$\mathrm{Br2(l) + 2NaI(aq) \rightarrow 2NaBr(aq) + I2(s)}$$



Formation of sodium chloride

5. Reactions with bases:

$$\mathrm{4F2(g) + 6NaOH(dilut) \rightarrow OF2(g) + 6NaF(aq) + 3H2O(l) + O2(g)}$$

Chlorine reacts with dilute sodium hydroxide to produce sodium chloride, sodium hypochlorate and water. The chemical equation for this reaction is as follows.

Cl2 in this case acts as an oxidant and a reducing agent. Such reactions are called disproportionation reactions:

Cl2(g) + 2NaOH(aq)(cold) → NaCl(aq) + NaClO(aq) + H2O(l)

Cl2 - 2e = 2Cl- | 1

Cl2 + 4OH- +2e = 2OCl- + 2H2O | 1

2Cl2 + 4OH- = 2OCl- + 2Cl- +2H2O

2Cl2 + 4NaOH = 2NaOCl + 2NaCl + 2H2O

3Cl2(g) + 6NaOH(aq)(hot) → 5NaCl(aq) + NaClO3(aq) + 3H2O(l)

With dry slaked lime, it gives bleaching powder.

2Ca(OH)2(aq) + 2Cl2(g) → Ca(OCl)2(aq) + CaCl2(aq) + 2H2O(l)

Ca(OH)2(aq) + Cl2(g) → CaOCl2(aq) + 2H2O(l)

6. Reactions with acids:

2F2(g) + 4HClO4(aq) → 4ClO3F(aq) + O2(g) + 2H2O(l)

F2(g) + HNO3(aq) → (NO2+)OF(aq) + HF(aq)

Br2(l) + H2S(conc) → 2HBr(conc) + S(s)

3I2(s) + 10HNO3(dilut.) → 6HIO3(aq) + 10NO(g) + 2H2O(l)

I2(s) + 10HNO3(conc hot.) → 2HIO3(aq) + 10NO2(g) + 4H2O(l)

Literacy

1. Which of the following are redox reactions? In each redox reaction, identify the element that is oxidized and the element that is reduced:

a) $Br_2(l) + H_2S(g) \rightarrow 2HBr(g) + S(g)$

b) $F_2(g) + 2NaCl(aq) \rightarrow 2NaF(aq) + Cl_2(g)$

c) $3Cl_2(g) + 2Fe(s) \rightarrow 2FeF_3(s)$

d) $4HCl(g) + MnO_2(s) \rightarrow MnCl_2(aq) + 2H_2O(l) + Cl_2(g)$

e) $2NaIO_3(aq) + 12HCl(conc) \rightarrow I_2(s) + 5Cl_2(g) + 2NaCl(aq) + 6H_2O(l)$

2. Why is iodine less reactive than other halogens at room temperature?

3. HF is less acidic than HI. Why?

4. Why is iodine I_2 a solid and Cl_2 a gas?

5. Why does F_2 act as a powerful oxidising agent?

Chemfact

The composition of bleaching powder is $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$.

Chemfact

Fluorine F_2 is an extremely strong oxidizing element, it reacts with iridium, platinum, plutonium, and curium to form IF_7, PtF_6, PuF_6, CmF_4.

Chemistry around us

Chlorine water on standing loses its yellow color due to the formation of HCl and HOCl. Hypochlorous acid (HOCl) so formed, gives oxygen which is responsible for oxidizing and bleaching properties of chlorine. Chlorine water is a powerful bleaching agent; bleaching action is due to oxidation.

Colored substance + O^* → Colorless substance

$Cl_2(g) + H_2O(l) \rightarrow 2HCl(aq) + O^*$

Terminology

- sea creature - теңіз жануарлары / морские животные;
- Chile saltpeter - чили селитрасы / чилийская селитра.

10.3 HYDROGEN CHLORIDE. HYDROCHLORIC ACID

How is HCl acid formed in our stomach? How does the stomach not digest itself if it has strong hydrochloric acid in it?

You will:

- understand the properties of hydrogen chloride and hydrochloric acid;
- understand the preparation and usage areas of hydrochloric acid

Glauber prepared this acid in 1648 by heating common salt with concentrated sulphuric acid. Davy in 1810 showed that it is a compound of hydrogen and chlorine.

Physical properties

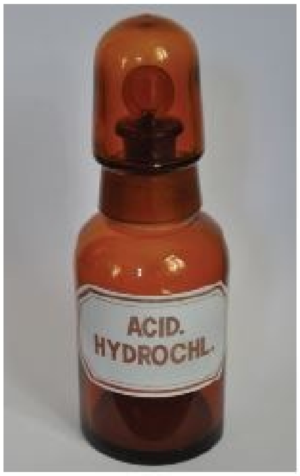
Hydrogen chloride is a colorless and pungent smelling gas. It is easily liquefied to a colorless liquid (b.p.-840C) and freezes to a white crystalline solid (f.p. -1140C). It is extremely soluble in water and ionises as below:

$$HCl + H2O \rightarrow H3O+ + Cl-$$

It doesn’t conduct electricity in its liquid and gaseous phases, only in its aqueous solutions.

An aqueous solution of hydrogen chloride is called hydrochloric acid. Hydrochloric acid is a strong acid. It can dissolve in organic solvents such as C_2H_5OH.

A 40 % HCl solution can be prepared with a density of 1.19 g/cm3. The concentrated HCl used in the laboratories is 35-36 %. It is a colorless acid with a sharp odor.




Rock salt

Industrial preparation

1. World production of HCl is of the order of 10 million tonnes. It is released from the rock-salt (Leblanc process):

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$

2. Hydrogen chloride is prepared by the direct reaction of hydrogen with chlorine, and its aqueous solution gives hydrochloric acid.

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Chemical properties

1. Reaction with metals

Hydrochloric acid reacts with active metals to produce the chloride salts and H_2 gas.

$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$

Passive metals does not react with dilute hydrochloric acid. But, adding bubbles of oxygen, reaction is occurs:

$4HCl(aq) + 2Cu(s) + O_2(g) \rightarrow 2CuCl_2(aq) + 2H_2O(l)$

2. Reaction with ammonia gas:

Solution of ammonia reacts with HCl acid solution to give ammonium chloride smog:

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(g)$

3. It reacts with bases, basic oxides and amphoteric oxides:

$2HCl(aq)+ MgO(s) \rightarrow MgCl_2(aq) + H_2(g)$

$6HCl(aq)+ Al_2O_3(s) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

$HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$

4. Hydrochloric acid reacts with some salts to produce other acids and insoluble chloride salts form. These types of reactions are used to detect some ions, such as Ag^+ and Pb^{2+}, in analytical chemistry.

$HCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + HNO_3(aq)$

$2HCl(aq) + Pb(NO_3)_2(aq) \rightarrow PbCl_2(s) + 2HNO_3(aq)$

$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

5. It reacts with oxidizing agents such as $KMnO_4$ (and $K_2Cr_2O_7$, $KClO_3$) to produce gas Cl_2:

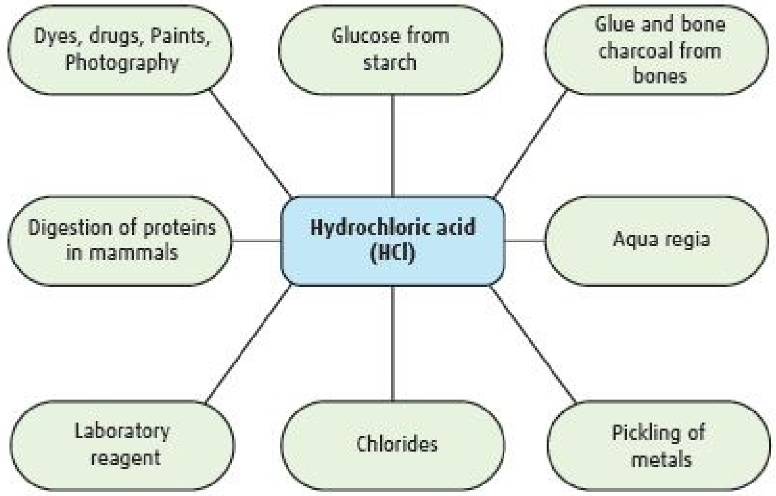
$$2KMnO_4(aq) + 16HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 8H_2O(l) + 5Cl_2(g)$$

6. When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, “king water” is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au(s) + HNO_3(conc) + 4HCl(conc) \rightarrow HAuCl_4(aq) + NO(g) + H_2O(l)$$

Uses

HCl is used in the manufacture of chlorine, NH_4Cl and glucose (from corn starch), for extracting glue from bones and purifying bone black, in medicine and as a laboratory reagent, in the manufacture of dyes, rubber and medicines. Also, it is found in our stomach for digestion. Most of the HCl is used for making vinyl chloride ($CH_2{=}CH{-}Cl$) and chlorinated solvents (CCl_4, CH_3Cl, CH_2Cl_2, etc).



Chemfact

$PbCl_2$ is a white crystalline solid (it looks like snow) that is almost insoluble in cold water. It is fairly soluble in hot water.

Chemistry around us

HCl is a major industrial chemical. Hydrochloric acid is used in the metal and chemical industries. In the metal industries, it is used to clean rust and scale from metal surfaces.

Literacy

1. What are the preparation reactions of hydrogen chloride?

2. Write the physical and chemical properties of hydrogen chloride.

3. Write the uses of HCl.

4. When 50 grams of an alloy of Cu and Al react with sufficient hydrochloric acid, HCl, 22.4 L of H2 at STP are produced. What is the mass percentage of Al in the alloy?

5. 17 g of calcium is reacted by concentrated HCl. Find the total volume of obtained gas at STP.

6. What mass of dilute hydrochloric acid solution containing 15% HCl will be needed to dissolve 36 g of calcium carbonate?

Terminology

- pungent smell - өткір иіс /острый запах;
- digestion - ас қорыту / пищеварение

10.4 HALIDES. BIOLOGICAL ROLE OF IODINE. USES OF HALOGENS AND THEIR COMPOUNDS

Why silver bromide AgBr (yellow precipitate) used in photography?

You will:

- determine the halide ions in given solutions;
- know uses of halogens and its compounds;
- determine the biological roles of halogens;
- provide qualitative analysis of halide ions.

Halides

The halogens react with metals to produce salts called metal halides (F-, Cl-, Br-, I-).

Important fluoride salts:

- - CaF2 - fluorspar - widely distributed mineral used as a flux in steelmaking and the production of HF.
- - HF - hydrogen fluoride - colorless, extremely toxic gas, used to make F2, organic fluorine compounds, and polymers. Also used in the aluminum manufacture and glass etching.

Important halogen salts:

- \- NaCl - sodium chloride - used in food industry, in the manufacture of chlorine, sodium, hydrochloric acid, sodium hydroxide and soda.
- \- KCl - potassium chloride - important potassium fertilizer
- \- ZnCl2 - zinc chloride - used in electrogalvanizing, in agriculture as pesticide, in cosmetics as skin cream
- \- CaCl2 - calcium chloride - used for refrigeration of plants, ice and dust control on roads, to preserve some foods as salt
- \- NaClO - sodium hypochlorite and Ca(CIO)2 calcium hypochlorite - oxidizing agents, used to bleach wood pulp and textiles and to disinfect swimming pools, foods, and sewage.
- \- NH4ClO4 - ammonium perchlorate - a strong oxidizing agent, used in the space shuttle as fuel.
- \- KClO4 - potassium perchlorate - for using in explosives and fireworks.
- \- AgBr - silver bromide is very sensitive to light. When they are exposed to sunlight, they are easily reduced to the metallic silver. As a result of this property, they are used to produce photographic films.
- \- KI - potassium iodide - added to table salt to prevent thyroid disease, used in chemical analysis

Fluorspar mineral

Biological role of iodine

Iodine belongs to the group of essential (vital) microelements. The main biological role of iodine is in the synthesis of thyroid hormones (thyroxin and triiodothyronine) through which it regulates: energy metabolism, body temperature, the rate of biochemical reactions, exchange of proteins, fats, water-electrolyte metabolism, metabolism of a number of vitamins.

Uses of halogens and its compounds

Fluorine is used in the manufacture of polymers such as teflon. F2 is component of freon gas (CCl2F2) used in refrigerators. it is used to decorate glassware.

Chlorine is used:

- - for bleaching wood pulp, bleaching cotton and textiles
- - in the extraction of gold and platinum
- - in the manufacture of dyes, drugs and organic compounds such as CCl4, CHCl3, DDT, refrigerants.
- - in sterilising drinking water

Bottles of Clorox bleach

Iodine is used as an antiseptic (tincture of iodine) in medicine and in halogen lamps in car headlights. The solutions of iodine in alcohols are used as an antiseptics in medicine. The compound iodoform (CHI3) is used as antiseptic in dentistry.

Iodine solution is used for detecting starch

Bromine is used in agriculture as drugs, in the manufacture of films and drug industry. Used to protect engines from knocking. Added to fuel-oil.

Lab work №2

Properties of halogens and qualitative analysis of halide-ions

Materials:

AgNO3, KCl, NaBr, KI, Pb(NO3)2, NaCl, KBr solutions, chlorine water, test tubes, teat pipette, burner, test tube holder.

Procedure:

Test 1. AgNO3

1. Put 5 ml of KCl(aq) in a test-tube and add five drops of AgNO3(aq). Leave for a few minutes.

2. Put 5 ml of NaBr(aq) in a test-tube and add five drops of AgNO3(aq). Leave for a few minutes.

3. Put 5 ml of KI(aq) in a test-tube and add five drops of AgNO3(aq). Leave for a few minutes.

Test 2. Chlorine water

1. Add a few drops of chlorine solution to 5 ml of NaBr(aq).

2. Add a few drops of chlorine solution to 5 ml of KI(aq).

Test 3. Pb(NO3)2

1. Put 5 ml of Pb(NO3)2(aq) into a boiling tube, then add five drops of NaCl(aq) to a boiling tube and heat till it boils.

2. Put 5 ml of Pb(NO3)2(aq) into a boiling tube, then add five drops of KBr(aq) to the boiling tube and heat till it boils.

3. Put 5 ml of Pb(NO3)2(aq) into a boiling tube, then add five drops of KI(aq) to a boiling tube and heat till it boils.

4. Place all 3 tubes in a beaker of cold water to cool.

Safety: Wear eye protection. Wear disposable gloves. Avoid skin contact. Wash hands after use.

Observation and questions:

1. Note your observations.

....

2. What can you say about the products of salts and salt reactions? Explain.

3. Write the ionic and net ionic reaction equations for the experiment.

Ionic equations :

....

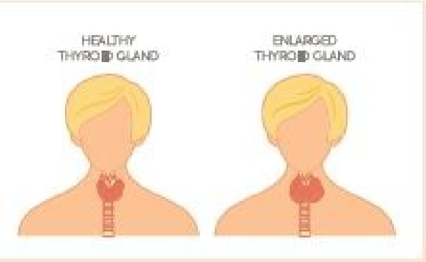
Net ionic equations :

....

4. Write colors of precipitates.

Chemistry around us

A deficiency of iodine in the body causes goiter.



Healthy woman and female with enlarged thyroid gland

Literacy

1. Write the products of electrolysis of the given substances.

- A. Molten potassium bromide
- B. Lithium chloride solution

2. If 67.2 L HBr gas (at STP) is completely dissolved in 25% NaOH solution (1 kg), find the mass percentages of all species in the final solution.

3. If 47.6 g of KBr is produced at the end of the reaction of potassium with bromine, how many grams of bromine are consumed?

Chemfact

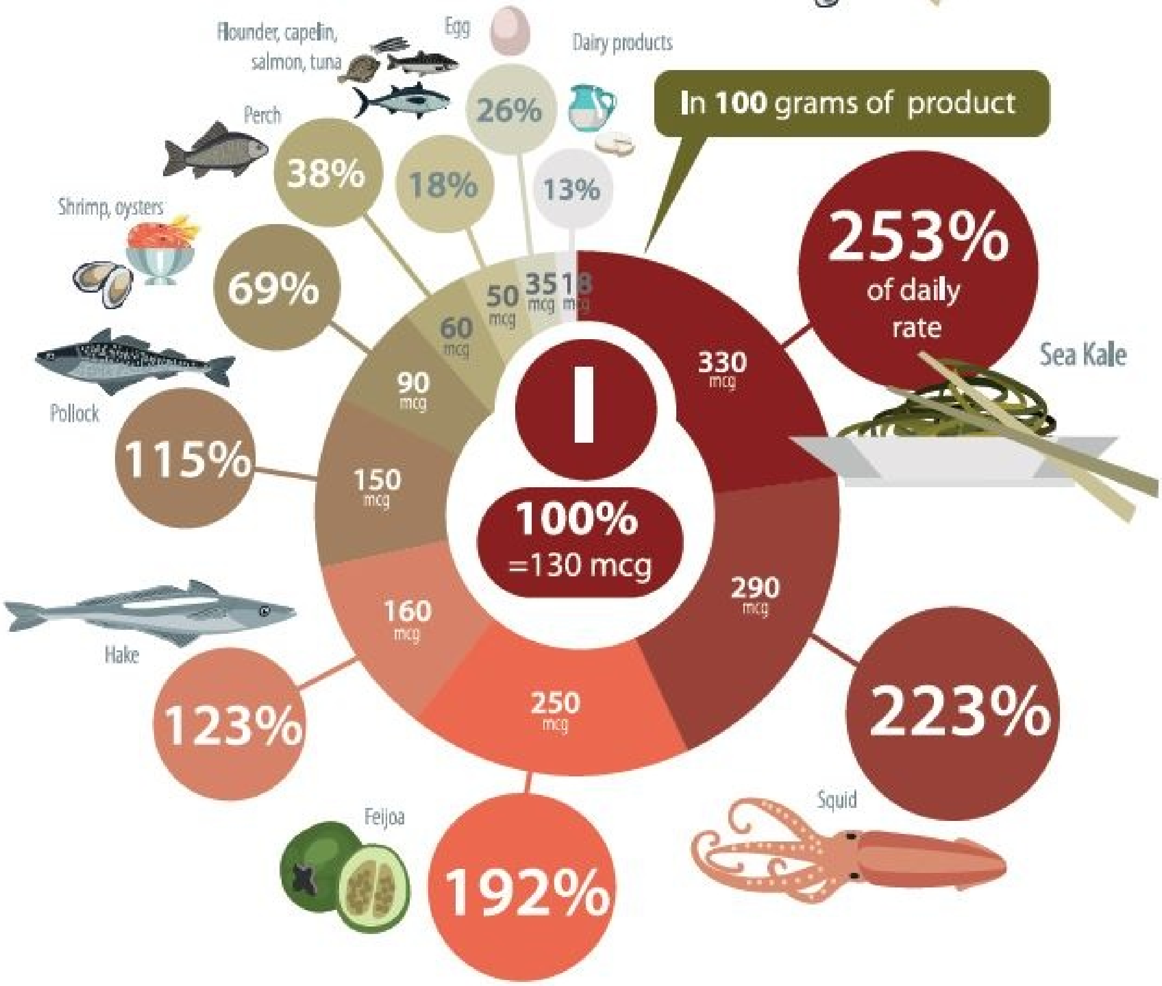
Chlorine was used for the preparation of poisonous gases such as phosgene ($COCl_2$), tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

On April 22, 1915, German forces introduced the use of lethal chlorine gas at Ypres, Belgium

Terminology

- halides - галогенидтер / галогениды;
- flux - ағын / поток;
- fluorspar - балқытқыш шпат / плавиковый шпат;
- goiter - кеңалқым, жемсау / зоб;
- tear gas - көз жасаурақыш газ / слезоточивый газ;
- mustard gas - иприт, қыша газы / горчичный газ, иприт.

Iodine food sources



QUESTIONS AND PROBLEMS

1. Discuss the general characteristics of Group 17 elements concerning their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity.

2. Discuss the trends in chemical reactivity of Group 17 elements.

3. Why does the reactivity of fluorine differ from chlorine?

4. How is fluorine prepared in the laboratory? Write the chemical equations.

5. Halogens exist as diatomic molecule. Why?

6. Why is chlorine a gas but iodine a solid?

7. Why are halogens strong oxidising agents?

8. Explain why fluorine forms only one oxoacid, HOF.

9. Write two uses of CaOCl2.

10. Write the reactions of F2 and Cl2 with water.

11. How can you prepare Br2 from HBr and HBr from Br2? Write chemical reactions.

12. What are the oxidation states of chlorine in the following:

HOCl, NaClO, ClF3, Cl2O7, Cl(O)F3

13. Write balanced equations for the following:

- - NaCl is heated with sulphuric acid in the presence of MnO2.
- - Chlorine gas is passed into a solution of KI in water.

14. The reaction below, which is chlorine with aluminum is exothermic.

2Al(s) + 3Cl2(l) → 2AlCl3(aq) ΔH = -703.4 kJ

How much heat is emitted when 36 g of Al reacts with excess Cl2?

15. What mass of CaBr2 is produced at the end of the reaction of 1.8 g of Ca with excess Br2 with 90% efficiency?

16. A mineral contains 17.29% sodium, 29.32% potassium and 53.38% chlorine in its structure. Find the chemical formula of this mineral.

17. Write the color of the following halogencompounds:

HF, CaF2, AgCl, AgBr, KClO3, Br2, KI, PbI2, PbCl2

18. These are three test tubes which are filled with NaCl, NaF and Pb(NO3)2 respectively. By using a halogenide solutions how can be found the given chemicals correctly? Explain.

19. This question concerns the inorganic compound, X, which contains sodium, chlorine and oxygen. X contains Na=21.6%; Cl=33.33%; O=45.07% by mass. Show the empirical formula of X. The relative molecular mass of X is 106.5. What is the molecular formula of X? Give the structural formula of X.

20. Silver bromide has been used as to produce photographic films. Silver bromide is 57.45% silver by mass. If you separate a 100 g sample of silver bromide into its elements, silver and bromine, how much silver would you have?

21. Balance the following equations, using the oxidation number method for the redox part of the equation.

- KI(aq)+ HNO3(aq) → I2(s)+ KNO3(aq) + NO(g) + H2O(l)

- MnO2 + HCl → MnCl2 + Cl2 + H2O
- NaOH + Cl2 → NaClO + NaCl + H2O

22. A 75.0 ml sample of 0.02 M Ba(OH)2 is neutralized by 82 ml of HCl. What is the molarity of the acid?

23. During a titration, 0.200M HBr is added to a KOH solution of unknown concentration. What is the concentration of the KOH solution if 20.0 ml of it is neutralized by 42.8 ml of the standard solution?

1. Write equilibrium expressions for the following reactions:

- - 4HBr(g) + O2(g) → 2Br2(g) + 2H2O(g)
- - NCl3(g) + Cl2(g) → NCl5(g)
- - PCl5(g) → PCl3(g) + Cl2(g)
- - CH4(g) + Cl2(g) → CH3Cl(g) + HCl(g)

2. At 793 K, the reaction H2 + Cl2 → 2HCl produces the following concentrations:

[H2]=3.49×10-4M; [Cl2]=0.80M; [HCl]=0.25M.

- What is the equilibrium constant expression for the reaction?
- What is the equilibrium constant for the reaction?

3. Calculate the amount of heat released in the complete combustion of 53 g of Al to form AlI3(s) at 25°C and 1 atm. ΔHf° for AlI3(s)=-627.6 kJ/mol.

Al(s) + I2(s) → AlI3(s)

4. Determine ΔS for the reaction

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(g)$,

given the following entropies.

Entropy ($HCl(g)$) = 186.8 J/(mol×K)

Entropy ($NH_3(g)$) = 192.6 J/(mol×K)

Entropy ($NH_4Cl(g)$) = 94.56 J/(mol×K)

5. What is the percent by mass of 98 g of potassium iodide dissolved in 1000 g of water?

6. What is the molarity of a solution that contains 45 g of sodium bromide dissolved in 580.0 mL of solution?

7. A mass of 101 g of potassium chlorate $KClO_3$ is dissolved in 480 g of water. What is the molality of the solution?

8. What happens when chlorine is passed through an aqueous solution of sodium hydroxide?

9. How is the presence of I_2 detected?

10. Mention three areas in which iodine plays an important role.

11. Although electron gain enthalpy of fluorine is less negative as compared to chlorine, fluorine is a stronger oxidising agent than chlorine. Why?

12. Sea is the greatest source of some halogens. Comment.

13. Name two poisonous gases which can be prepared with chlorine gas.

14. Write the reaction equations for the following reaction schemas.

- KCl → HCl → Cl2 → Br2 → HBrO → HBr → KBr
- HCl → NaCl → Cl2 → NaClO → NaClO3
- KMnO4 → I2 → HIO3 → KIO3 → KI → I2 → NaIO3
- SiO2 → SiF4 → HF → NaF

11 CHAPTER

ALKALINE EARTH METALS

CHAPTER 11: ALKALINE EARTH METALS

11.1 ALKALINE EARTH METALS AND THEIR PROPERTIES

Why statues and buildings in industrial cities have a tendency to break down faster than those located in rural areas?

You will:

- know general properties of group 2 elements;
- explain the patterns of changes in physical and chemical properties of group 2 elements.

Group 2 elements are called alkaline earth metals. Its members are beryllium, magnesium, calcium, strontium, barium and radium.

Electron configuration

The group 2 elements have two electrons in their outermost shell. Their general electron configurations may be represented as [noble gas] ns2. Compounds of these elements show ionic properties.

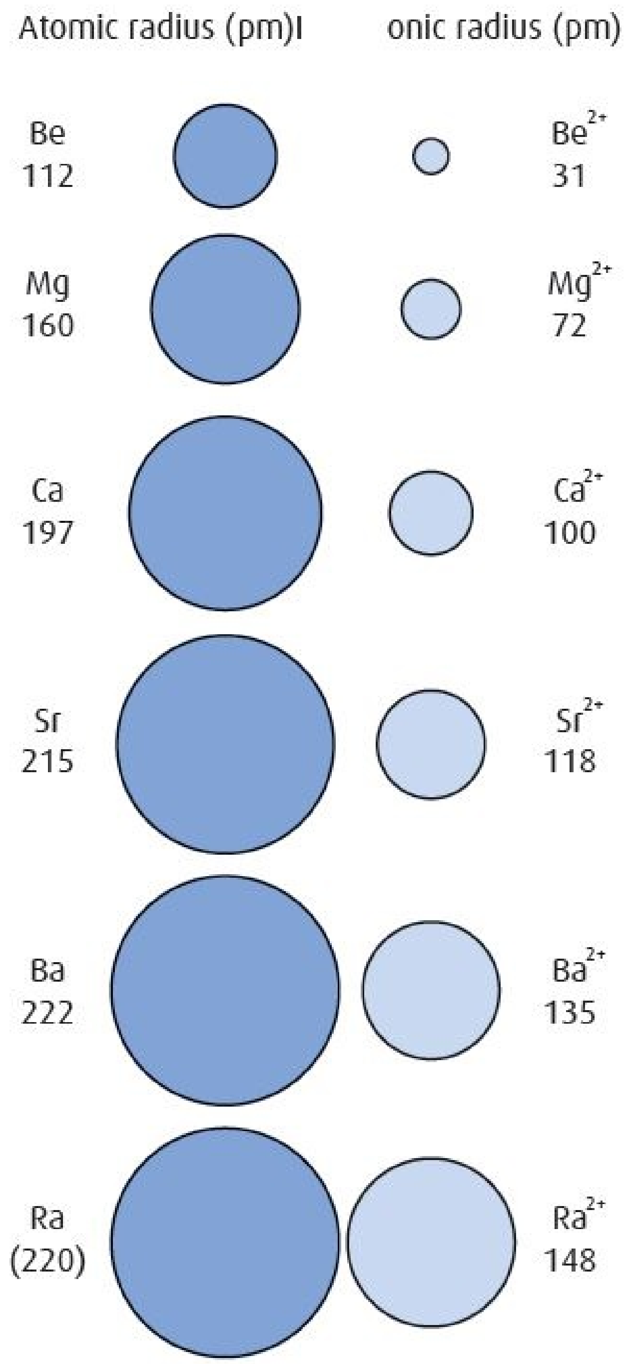
Atomic and Ionic Radii

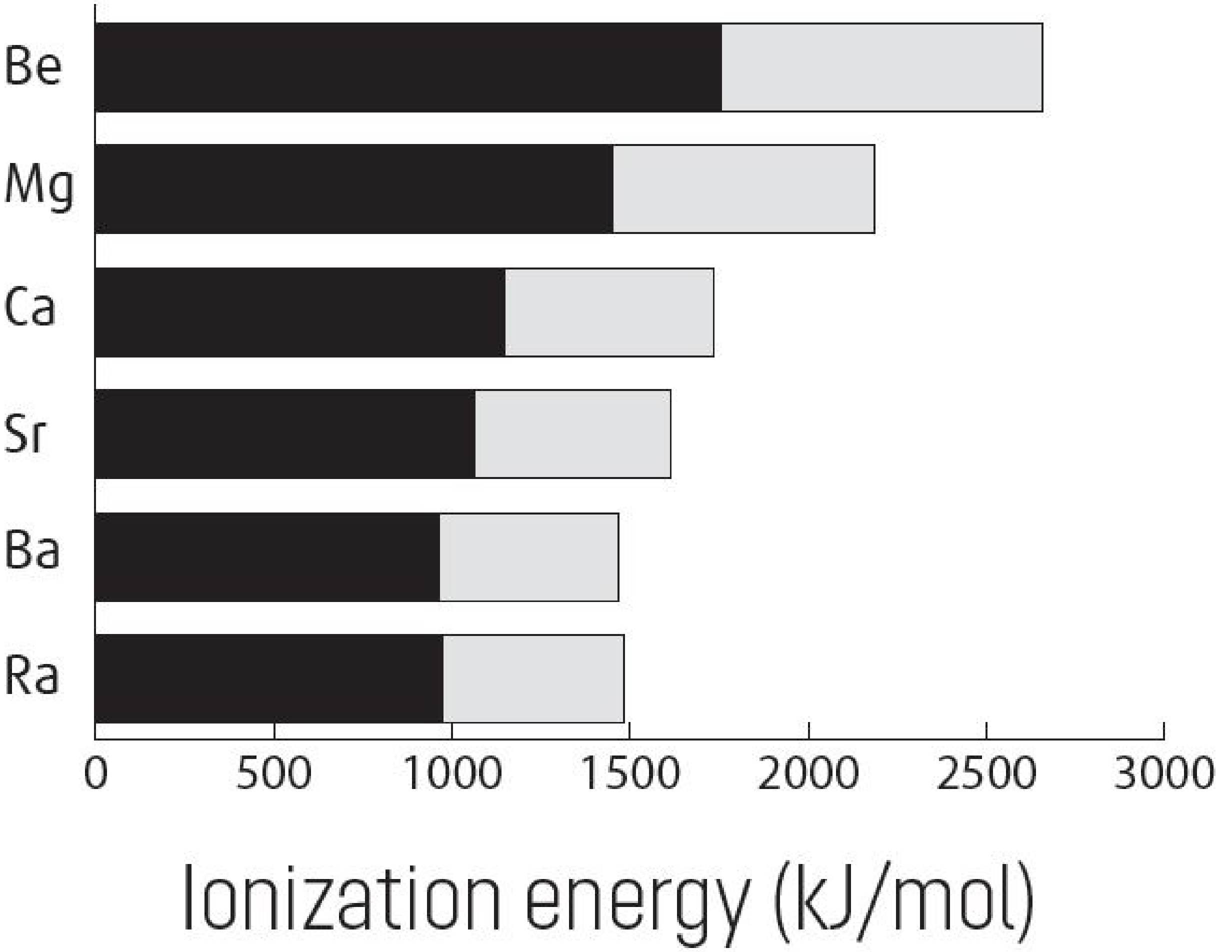
Atomic and ionic radii of group 2 elements increase within a group with an increase in atomic number.

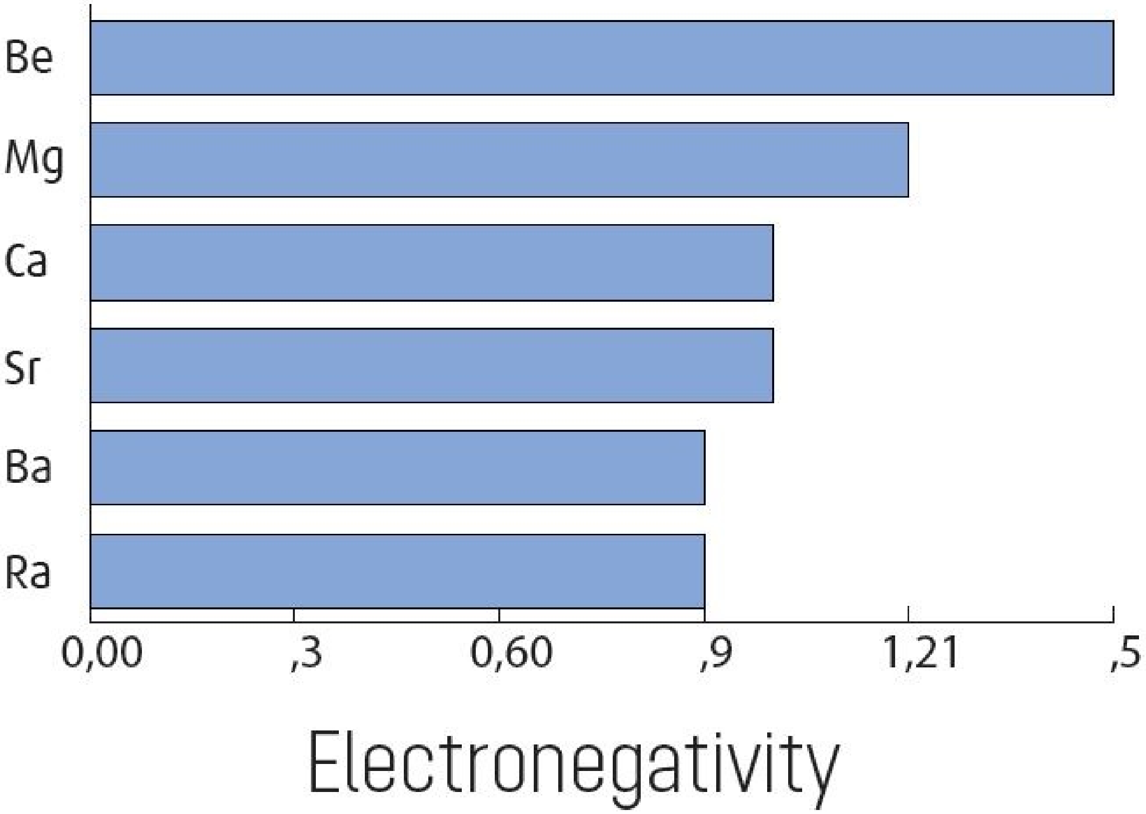
Due to the large size of alkaline earth metals, they have low ionization enthalpies. Moreover, as the atomic size increases the ionization enthalpy decreases.

Within the group the ionization energies of alkaline earth metal ions decrease:

Be > Mg > Ca > Sr > Ba


Atomic radius (pm)I
onic radius (pm)
Be
112
Be2+
31
Mg
160
Mg2+
72
Ca
197
Ca2+
100
Sr
215
Sr2+
118
Ba
222
Ba2+
135
Ra
(220)
Ra2+
148


Be
Mg
Ca
Sr
Ba
Ra
0
500
1000
1500
2000
2500
3000
Ionization energy (kJ/mol)

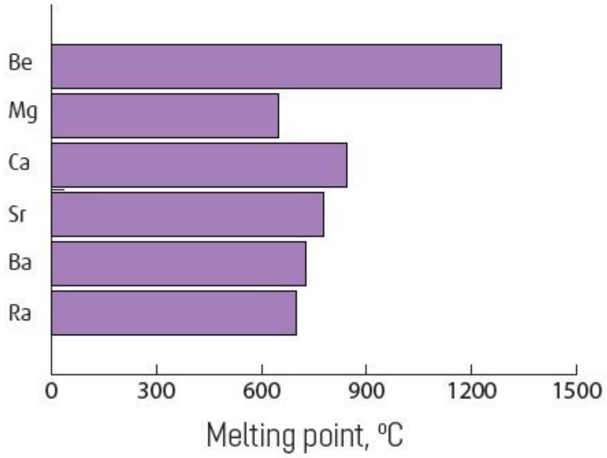


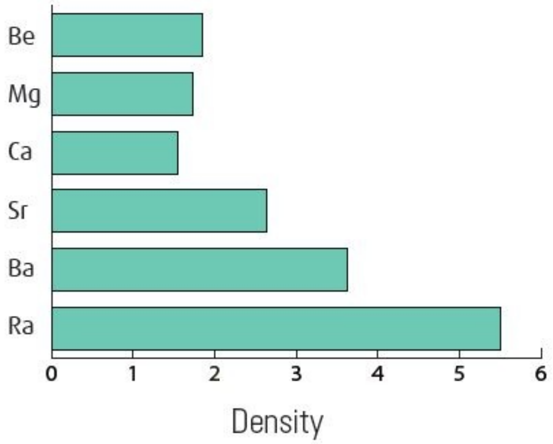
Physical Properties

Generally, the group 2 elements are shiny silvery white colored metals. Colors of beryllium and magnesium are differ from other group members, they are somewhat greyish. They are relatively harder and their melting and boiling points are higher than those of alkali metals due to smaller sizes.

Table 16 *Physical Properties of Alkaline Earth Metals*

Properties	Be	Mg	Ca	Sr	Ba	Ra
Atomic number	4	12	20	38	56	88
Atomic mass	9.01	24.31	40.08	87.62	137.33	226.03
Electron configuration	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$	$[Rn]7s^2$
Melting point, °C	1287	650	842	777	727	700
Boiling point, °C	2471	1090	1484	1382	1897	1140
Density, g/cm^3	1.84	1.74	1.55	2.63	3.59	(5.5)





As metal ions exposed to flame, electrons of that metal can be excited to higher state, so that when it reverts to its previous state it emits energy in the form of visible light. Flame test analysis can be used in detecting these ions qualitatively and determining concentrations of these ions by flame photometry

Table 17 *Flame colors of Alkaline Earth Metals*

Metals	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Flame color	white	-	brick red	crimson red	apple green

Chemical Properties

The alkaline earth metals are the most reactive metals after group 1 elements. The reactivity of these elements increases going down the group. The alkaline earth metals burn in air with bright flame. As the result, their oxides and nitrides are formed.

Compounds of the alkaline earth metals are similar in composition, they all form oxides MO, hydroxides M(OH)2, carbonates MCO3, sulfates MSO4, and others (M is any alkaline earth metal).

1. All alkaline earth metals, except Be, react with H2 gas in hot medium to produce hydrides:

Mg(s) + H2(g) → MgH2(s)

2. Ca, Sr and Ba react with water to produce metal hydroxides and hydrogen gas:

Ca(s) + 2H2O(l) → Ca(OH)2(aq) + H2(g)

Magnesium metal reacts slowly with boiling water. The reaction of beryllium with water is very difficult.

3. Group 2 elements reduce O2, N2 to form the oxides and nitrides:

2Sr(s) + O2(g) → 2SrO(s)

3Sr(s) + N2(g) → Sr3N2(s)

4. They react with halogens to produce metal halides.

Ba(s) + Cl2(g) → BaCl2(g)

5. They readily react with acids:

Be(s) + 2HCl(aq) → BeCl2(aq) + H2(g)

The reaction of Mg with nitric acid HNO3 produces N2O, NO2 gases:

4Mg(s) + 10HNO3(dilut) → 4Mg(NO3)2(aq) + N2O(g) + 5H2O(l)

4Mg(s) + 10HNO3(conc) → 4Mg(NO3)2(aq) + NO2(g) + 5H2O(l)

6. All oxides and hydroxides of alkaline earth metals show basic properties, except beryllium which oxide and hydroxide show amphoteric properties.

$Be(s) + 2HCl(aq) \rightarrow BeCl_2(aq) + H_2(g)$

$Be(s) + 2NaOH(aq) + 2H_2O(l) \rightarrow Na_2[Be(OH)_4](aq) + H_2(g)$

Literacy

1. Melting points of alkaline earth metals are higher than the alkali metals. Explain.

2. Where we use barium sulfate $BaSO_4$?

3. Why are barium and strontium used in fireworks?

4. Explain why magnesium reacts slowly with water

5. Write balanced equations for

- - the preparation of slaked lime from marble
- - the preparation of magnesium from “white magnesia”
- - the use of slaked lime to remove CO_2

6. Write the electron configuration of Ba and Be.

Chemistry around us

Metallic beryllium is used to prepare special alloys. About 2% beryllium in copper produces a hard alloy especially suited for use in springs.

Chemfact

Strontium has many important applications in industry. The salts of strontium are used in signal rockets and fireworks to produce red light.

Chemistry around us

Radium is used in self luminous paints and in radiotherapy and as a neutron source.

Radiotherapy treatment

Terminology

- predominantly - айырықша, басым / преимущественно;
- estimation - есептеу / вычисление;
- penetrate - ену, өту / проникать;
- disappear - жоғалу / исчезнуть;
- luminous - жарқыраған / светящийся.

11.2 IMPORTANT COMPOUNDS OF ALKALINE EARTH METALS. CARBONATES

Marble, limestone, chalk, pearls, seashells represented by the same chemical formula $CaCO_3$. Why are they physically different?

You will:

- name the application areas of the important compounds of alkaline earth metals;
- draw the carbonate cycle in nature and name the application areas of carbonates;
- plan and conduct an experiment on the qualitative determination of metal cations of the 2nd group.

Occurrence

Since the group 2 elements are relatively active metals, they occur as compounds in nature.

Beryllium occurs in a trace amount in nature. The most important ores of beryllium is beryl, alexandrite, lazurite, emerald ($Be_3Al_2(SiO_3)_6$). The principal useful ores of magnesium are magnesite $MgCO_3$, dolomite $CaCO_3 \cdot MgCO_3$(a double salt), asbestos $Mg_3Si_2O_7 \cdot 2H_2O$; carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ and Epsom salt $MgSO_4 \cdot 7H_2O$ are found in mineral water. Epsom salt is used as a and as a filler for cotton goods.


Alexandrite mineral


Lazurite mineral


Emerald mineral


Asbestos roofs


Magnesite mineral

Calcium compounds are widely distributed in nature, occurring as limestone or marble CaCO3, gypsum CaSO4·2H2O, apatite, and fluorite CaF2. Salts of sulfate, silicate and phosphate are also found in the Earth's crust.

Strontium, barium, radium are found in trace amounts in nature. All the isotopes of radium are radioactive. The isotope 226Ra is the most stable isotope with a 1600 year half-life.


Purple apatite (calcium phosphate) mineral


Baryte mineral

The compounds of alkaline earth metals are ionic. They have high melting and boiling points. They are thermally stable. Their salts are less soluble in water than those of alkali metals. Solubilities of alkaline earth metal salts increase from beryllium to barium. Most of the compounds of beryllium and some compounds of magnesium show a tendency to covalency, so they differ from other compounds in the group.

General characteristics of compounds of the alkaline earth metals

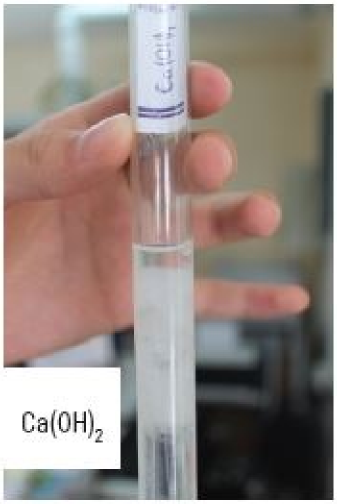
Oxides of alkaline earth metals are formed when metals are burnt in oxygen. Apart from BeO, all alkaline earth metal oxides show basic properties. Therefore, when the oxides are dissolved in water they produce bases. As the atomic number increases, solubility and basicity of alkaline earth metal hydroxides also increase.

Carbonates of alkaline earth metals can be precipitated from their soluble salt solutions by adding soluble carbonates such as sodium and potassium. As we go down the group, the solubility of carbonates in water decreases. Decomposition of these carbonates, forming carbon dioxide and metal oxide can be observed when they are heated.

$MCO3(s) \rightarrow MO(s) + CO2(g)$

Nitrates of alkaline earth metals decompose when heated by releasing metal nitrite and oxygen. As atomic number of these metals increase they become more heat-resistant, so higher temperatures are required to decompose barium nitrate compared to calcium nitrate.

$M(NO3)2(s) \rightarrow M(NO2)2(s) + O2(g)$



Some important compounds of calcium

Important compounds of calcium are calcium oxide, calcium hydroxide, calcium sulfate, calcium carbonate and cement. These are industrially important compounds.

Calcium oxide (lime) is used in the production of cement and is obtained by heating calcium carbonate (limestone) at 900°C.

CaCO3(s) → CaO(s) + CO2(g)

Addition of calcium oxide to water is called slaking, and the product, Ca(OH)2, is called slaked lime (lime water).

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

$Ca(OH)_2$ is used in the preparation of mortar (slaked lime plus sand) which sets to a solid by reconversion of the $Ca(OH)_2$ to $CaCO_3$ as a result of the reaction with CO_2 in the air.

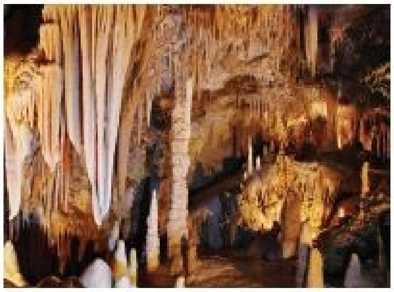
$Ca(OH)_2(s) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

Calcium carbonate occurs naturally as marble, limestone, chalk and calcite. As mentioned above, it forms by evolving CO_2 gas into $Ca(OH)_2$ solution. Underground water containing CO_2 dissolve some amount of $CaCO_3$ and the equilibrium below is established.

$CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca(HCO_3)_2(aq)$

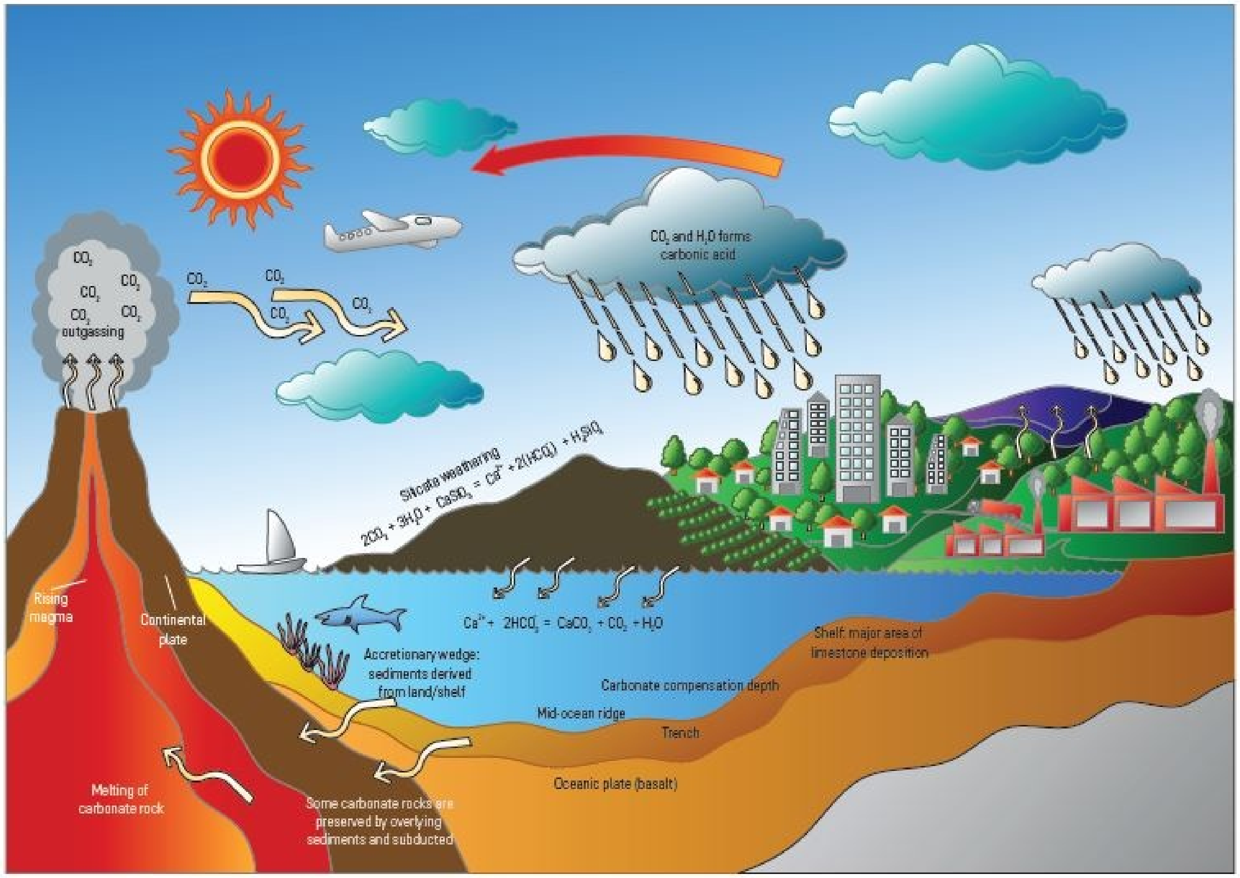
When such underground water reaches the earth's surface, the pressure on it decreases. Because of the decrease in solubility of CO_2 in water, the equilibrium reaction shift s to the left , that is, the $CaCO_3$ precipitate is formed. Formation of stalactites and stalagmites is a good example of this process.

Gypsum statue



Stalactites and stalagmites in a cave

Among the best-known deposits of phosphates are the Karatau Ridge, Mangystau and Aktobe region. Zhambyl region is the gypsum producing area in the country. Kostanay region is rich in minerals of dolomite.



Carbonate cycle in nature

Keep in mind

Mg(OH)2, milk of magnesia is used as a stomach antacid.

Literacy

1. Characterize the following compounds as soluble or insoluble in water: CaCO3, CaSO4, BaCl2, Ba(OH)2, Mg(OH)2, MgCO3.

2. Write ionic and net ionic equations for the following reactions:

- - CaCO3 + H2SO4 →
- - BaCl2 + Na2CO3 →

3. Which of the following processes will likely result in a precipitation reaction?

- - mixing an H3PO4 solution with a Ca(OH)2 solution.
- - mixing a HF solution with a CaCl2 solution.
- - mixing a K2SO4 solution with a Ba(OH)2 solution.

4. Suggest one method by which you might separate

- - Ca2+ from Cu2+
- - NH4+ from Ca2+

5. Calcium oxide is used in cement industry:

CaCO3(s) → CaO(s) + CO2(g)

Calculate the yearly release of carbon dioxide CO2 (in m3) to the atmosphere if the annual production of calcium oxide in Kazakhstan is 1.25×108 kg.

lab work №3

Properties of group 2 elements and their compounds

Decomposition of carbonates

Materials:

calcium carbonate (chalk and marble), distilled water, test tubes, indicator (litmus or universal), burner, round bottom flask.

Procedure:

1. Put calcium carbonate into the test tube.

2. Fill round bottom flask with distilled water.

3. Construct set of laboratory equipments as shown in the picture.

4. Heat the test tube with calcium carbonate gently using a burner. Observe the changes taking place in the tube.

5. Stop heating when releasing of the gas finishes.

6. Provide qualitative reaction for carbon dioxide using indicator.

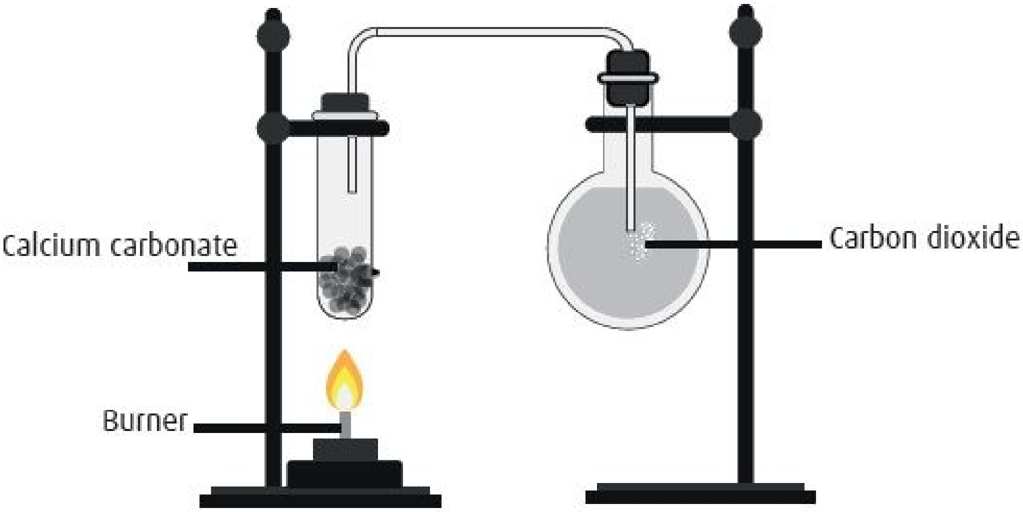
7. Dissolve calcium oxide in distilled water and check it with an indicator.

Conclusion and questions:

1. Note your observations

2. Write chemical equations.

3. Explain changes of colors of indicators



Flame test

Materials:

salts of calcium, barium and strontium, distilled water, wood sticks, burner, flask.

Procedure:

1. Place 5 g of salts of calcium, barium and strontium in three different flasks. Pour 50 ml of distilled water in all of them. Stir them.

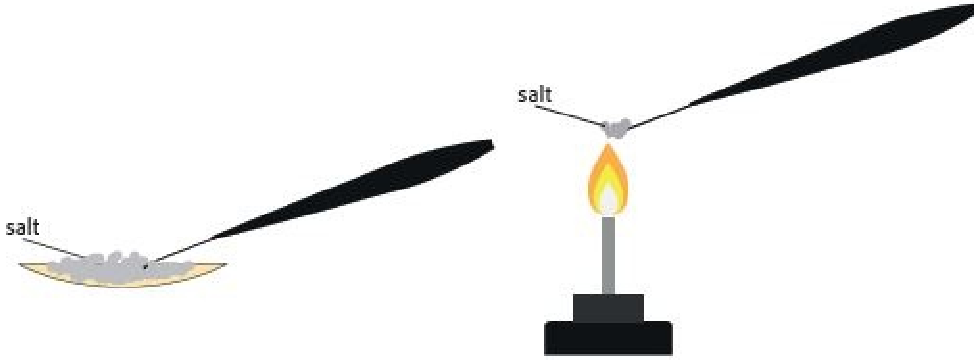
2. Put wood sticks in each flask. Leave it for somewhile.

3. Place each stick in the flame of the burner.

4. Observe color changes.

Conclusion and questions:

1. Complete the following table



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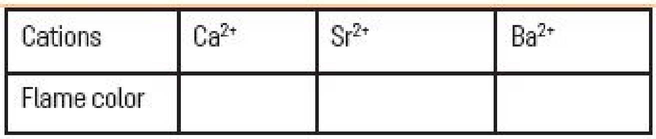


Cations	Ca^{2+}	Sr^{2+}	Ba^{2+}
Flame color			

2. Is it possible to use the flame test to distinguish metals in a sample? Explain.

Reactions of alkaline earth metals with oxygen

Materials:

test tube, magnesium ribbon, burner, tweezers, stands and clamps.

Procedure:

1. Take 0.5 - 2 g of magnesium ribbon with tweezers.

2. Place it into the flame of the burner.

3. Observe formation of light.

Observation and questions.

1. Write the chemical equation of the reaction.

2. Measure the mass of the formed magnesium oxide.

3. Calculate the yield of the reaction.

Practice work №2

Solving experimental problems

Materials:

10 g of calcium turnings, 100 ml of distilled water, beaker 250 ml.

Procedure and calculations

Step 1

Calculate mole number of calcium in a sample. Show your calculations below:

____ mol Ca.

Mass of water _________ g H2O.

Write the reaction of calcium with water:

____

How many grams of water reacts with calcium?
__________________ g H2O.

Mass of produced hydrogen gas _________________ g H2.

Volume of produced hydrogen gas at STP _________________ L H2.

Mass of produced calcium hydroxide: ________________ g Ca(OH)2.

Molarity of produced calcium hydroxide solution: __________M Ca(OH)2.

Materials:

sodium carbonate powder, Erlenmeyer flask 250 ml, distilled water, filter paper, scale.

Step 2

Prepare 0.25 M sodium carbonate solution. Dissolve __________ g of sodium carbonate in 200 ml of water.

Find mole number of sodium carbonate in the solution: __________ mol Na2CO3.

Pour sodium carbonate solution into the calcium hydroxide solution prepared in step 1.

Write the reaction of calcium hydroxide with sodium carbonate solution:

____

Find theoretical mass of calcium carbonate precipitate: ______________ g CaCO3.

Filter the formed precipitate and weigh the mass of CaCO3.

Actual mass of calcium carbonate precipitate: __________________ g CaCO3.

Step 3

Find percent yield of chemical reaction by formula:

ŋ = (actual mass) × 100% /(theoretical mass)

ŋ = ___________%.

Conclusion and questions:

1. What happens when you add calcium metal to water in the beaker?

2. What color results when phenolphthalein indicator is added to the solution in which calcium is reacting?

3. What is the compound that exists in the solution after step 2?

4. Why is the actual mass less than the theoretical mass?

Terminology

- lime - сөндірілмеген әк / негашеная известь;
- slaked lime (lime water) - сөндірілген әк / гашеная известь;
- limestone - әктас / известняк;
- emerald - зүмірет, зүбәржат / изумруд;
- asbestos - асбест / асбест;
- Epsom salt - ащы (ағылшын) тұз / английская соль.

QUESTIONS AND PROBLEMS

1. What are the common physical and chemical features of alkaline earth metals?

2. Discuss the general characteristics (properties) of alkaline earth metals.

3. Write the electron configuration of $_{12}Mg$.

4. Which compound of alkaline earth metals is used as a purgative?

5. Which element is the hardest in the alkaline earth metals group?

6. Which member of group 2 is radioactive?

7. Find out the oxidation state of barium in BaO2.

8. Explain why magnesium is less reactive than calcium.

9. Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so. Why?

10. What happens when

- - magnesium is burnt in air
- - quicklime is heated with silica
- - chlorine reacts with slaked lime
- - calcium nitrate is heated ?

11. Describe two important uses of each of the following: magnesium milk, calcium milk, quicklime.

12. Draw the structure of BaCl2 and MgCl2.

13. Draw the structure of BaSO4 and Ca(OH)2.

14. The carbonates and sulfates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are slightly soluble in water. Explain.

15. Describe the importance of the following compounds: barium sulfate, cement, gypsum.

16. What happens when

- - beryllium metal is dropped in water?
- - magnesium metal is heated in free supply of air?
- - calcium hydride dissolves in water?

17. Explain why

- - is a solution of Ca(NO3)2 neutral?
- - are alkaline earth metals prepared by electrolysis of their fused chlorides?
- - is calcium found to be more useful than magnesium?

18. Write balanced equations for the reactions between

- - Be and NaOH solution
- - Ca and water
- - CaCl2 and Na2CO3

19. Which of the following alkali metals has the lowest melting point?

- - Be - Sr
- - Ba - Ca

20. Which one of the following metals gives hydrated salts?

- - Ca - Ba
- - Sr - Cu
- - Fe - Li - Na

21. What mass of CaH_2 is produced at the end of the reaction of 22 g of Ca with excess H_2?

22. What mass of BaO is produced at the end of the reaction of 128 g of barium with excess O_2?

23. What mass of calcium reacts with excess water to produce 78 g of $Ca(OH)_2$?

24. What mass of beryllium reacts with excess NaOH solution to produce 4.48 L of H_2 gas?

25. What volume of N_2O gas is produced at the end of the reaction of 2.4 g of Mg with 90 g of diluted HNO_3 15% by mass at STP?

26. What volume of H_2 gas is produced at the end of the reaction of 45 g of Sr with 73 g of HCl at STP?

27. Write the chemical equations for each step in following reaction schemas.

- $Be \rightarrow Na_2BeO_2 \rightarrow Be(NO_3)_2 \rightarrow Be(OH)_2 \rightarrow Na_2[Be(OH)_4] \rightarrow BeCl_2$
- $Ca \rightarrow Ca_3P_2 \rightarrow Ca(OH)_2 \rightarrow CaO \rightarrow CaCO_3 \rightarrow Ca(HCO_3)_2 \rightarrow CaSO_4$

28. Write the chemical equations for each step in followings

- $CaC_2 \rightarrow Ca(OH)_2 \rightarrow CaO \rightarrow CaCl_2 \rightarrow Ca(OH)_2 \rightarrow CaOCl_2 \rightarrow CaCl_2$
- $BaH_2 \rightarrow Ba(OH)_2 \rightarrow BaCl_2 \rightarrow BaCO_3 \rightarrow BaSO_4$

29. Find the alkaline earth metal that has given the properties.

- - All its electrons are found in s orbitals.
- - It is radioactive.
- - Its properties are similar to those of aluminum.
- - It is found in chlorophyll.

- - It is very inert to water.
- - Its compounds are widely used in building.
- - It causes water hardness and doesn't react with cold H2SO4

30. The solubility of barium hydroxide, Ca(OH)2, at 25°C is 0.185 g/L.

Calculate the molar concentration of the saturated aqueous solution. If it is assumed that the solute is completely ionized, calculate the hydroxide ion concentration of the solution.

31. A student preparing a solution for an experiment measured the weight of the sample solute to be used. If she is supposed to use 1.5 moles of sodium hydroxide, she must use:

- - 8 g of solute
- - 40 g of solute
- - 80 g of solute
- - 160 g of solute

32. Which of the followings best represents the total number of atoms present in a sample of magnesium metal weighing 80 g?

- - 1×1023
- - 6.02×1023
- - 3.01×1023
- - 2×1023

33. Choose the best value that corresponds to the percentage composition of iodine in barium iodide?

- - 53.87%
- - 45.12%
- - 19.55%
- - 46.13%

34. A student researcher analyzing the identity of the by product of a reaction found that the compound contained 29.41%

calcium, 23.53% sulfur and 47.06% oxygen. What is the most likely formula of this compound?

- \- $CaCO3$
- \- $CaSO4$
- \- $CaSO3$
- \- CaS

35. A reaction mixture contains 80.75 g magnesium and 96 g bromine. Predict the limiting reagent if the reaction occurs as shown below.

$Mg + Br2 \rightarrow MgBr2$

36. A student conducted the described reaction below in a lab as a part of her research assignment. She used 49.2 g of calcium nitrate, with excess of sodium carbonate. What is the percent yield of $CaCO3$ precipitate, if the actual yield of $CaCO3$ was 28 g?

37. Arrange the following elements in terms of increasing atomic radius:

- \- Mg, K, Cl, Ba
- \- Cl, Mg, K, Ba
- \- Cl, K, Mg, Ba
- \- Ba, K, Mg, Cl
- \- Mg, K, Cl, Ba

38. Which one of the following elements belongs to the s block in the periodic table?

- \- Fe
- \- Co
- \- Al
- \- Ba

39. Calculate the molarity of a solution that contains 36.2 g of $Mg(NO3)2$ in 3 liters of solution.

40. Calculate the ΔH of the reaction between Mg_3N_2 and water, forming $Mg(OH)_2$ and NH_3. The enthalpies of the related reactions are also given.

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

$\Delta H_f(Mg_3N_2) = -461.1$ kJ/mol

$\Delta H_f(H_2O) = -285.8$ kJ/mol

$\Delta H_f(Mg(OH)_2) = -924.7$ kJ/mol

$\Delta H_f(NH_3) = -46.2$ kJ/mol

41. Why does the solubility of alkaline earth metal carbonates and sulphates in water decrease down the group?

42. A 36 g mixture of Mg and Ca is reacted with Br_2 at high temperatures. A 212 g mixture of metal bromides are produced. What is the percentage of the mass composition of the original mixture?

43. When 6 g of the alloy of Cu and Mg react with sufficient amount of HCl, 2.24 L of H_2 at STP are produced. What is the percentage of copper in the alloy?

44. When a 6.1 g mixture of $CaCO_3$ and $NaHCO_3$ is heated 2.31 g of CO_2 and 0.225 g of H_2O are produced according to the reactions:

$CaCO_3 \rightarrow CaO + CO_2$

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

Find the mass of $CaCO_3$ in the mixture.

45. A 20.8 g mixture of Mg and Ca is reacted with water. A 41.2 g mixture of metal hydroxides are produced. What is the

percentage of magnesium?

12
CHAPTER

ORGANIC CHEMISTRY

CHAPTER 12: ORGANIC CHEMISTRY

12.1 INTRODUCTION TO ORGANIC CHEMISTRY

Why number of organic compounds is much bigger than of inorganic?

You will:

- understand organic chemistry as chemistry of hydrocarbons and their derivatives;
- differentiate empirical, molecular, structural and spatial formulas of hydrocarbons;
- derive simplest and molecular formulas of organic compounds according to mass percentage of elements and relative density of their vapors.

Organic chemistry

The main element in the composition of organic compounds is carbon, which can combine with almost all chemical elements to form molecules of chain and cyclic structures of various sizes. Many consider organic chemistry the chemistry of carbon compounds. However, not all carbon compounds are organic, for example, carbon oxides, carbonic acid, its salts - carbonates and hydrogen carbonates, metal carbides and some other compounds are inorganic substances. A qualitative feature of the subject of organic chemistry is the study not of carbon itself, but of hydrocarbons and their derivatives. Therefore, the following definition is more accurate: organic chemistry is the chemistry of hydrocarbons and their derivatives.

Structural theory of organic compounds

Structural theory of organic compounds is the theory of chemical structure, developed by Russian chemist A.M. Butlerov in the XIX century. The main postulates of the structural theory of organic compounds:

1. Atoms in molecules are connected to each other in a certain sequence according to their valencies. The sequence of interatomic bonds in a molecule is called its chemical structure and is reflected by a single structural formula.

2. Chemical structure can be established by chemical methods. (At present, modern physical methods are also used).

3. The properties of substances depend on their chemical structure.

4. By the properties of a given substance, we can determine the structure of its molecule, and according to the structure of a molecule, it is possible to foresee properties.

5. Atoms and groups of atoms in a molecule have mutual influence on each other.

Formula concept in organic chemistry

We know that a chemical formula shows the numbers and types of atoms in a compound.

When we look at a chemical formula of an inorganic compound, the number of atoms and the types of bonding can easily be inferred. In inorganic compounds there are no other compounds with the same formula. NaCl represents sodium chloride and there is no other compound which is shown by this formula.

Organic chemistry, oppositely, contain many different compounds which have the same number and type of atoms. For example, C_5H_{12} may be the symbol of three different compounds, and there are 14 different compounds which have the formula $C_5H_{12}O$.

Although the numbers of atoms of these compounds are the same,their physical and chemical properties differ. For this reason, it is necessary to show the structures of compounds in organic chemistry.

There are three ways to write a formula in organic chemistry.

A petroleum refinery. Petroleum, along with natural gas, provides nearly 90% of the organic raw materials for the synthesis and manufacture of synthetic fibers, plastics, detergents, drugs, dyes, adhesives, and a multitude of other products.

Empirical Formula

Empirical formula indicates the type and ratio of atoms in a compound. It doesn't necessarily show the correct number of atoms and so the exact structure of a compound may not be understood when using this formula.

For example; CH may represent either C2H2 or C6H6

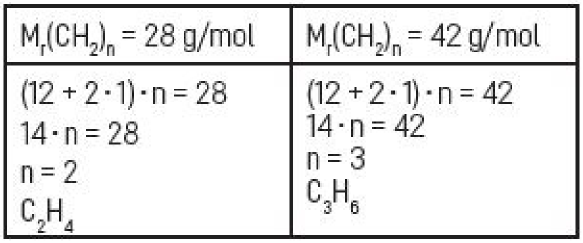
Molecular Formula

Molecular formula shows the actual number of atoms in a compound. “n” is an integer; 1, 2, 3……

For (CH2)n if n = 2 then the molecular formula is C2H4; if it is 3 the molecular formula will be C3H6.

When we know the empirical formula and atomic weight of a compound, molecular formula can be determined for that compound.

For example.

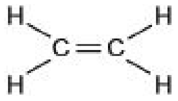


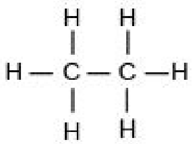
$M_r(CH_2)_n = 28$ g/mol	$M_r(CH_2)_n = 42$ g/mol
$(12 + 2 \cdot 1) \cdot n = 28$ $14 \cdot n = 28$ $n = 2$ C_2H_4	$(12 + 2 \cdot 1) \cdot n = 42$ $14 \cdot n = 42$ $n = 3$ C_3H_6

Structural Formula

Although a molecular formula shows the number of atoms in a compound, it does not show the type of bonding between atoms. We can show how atoms are bonded to each other by using structural formula.

Such as





If there is more than one group that is bonded to the same central atom, the groups may be written in parentheses and number of the groups written outside the parentheses as a subscript.

Chemistry around us

Chemists obtain organic compounds in two principal ways: isolation from nature and synthesis in the laboratory.

Literacy

1. How do we write structural formulas of organic compounds?

2. List the four principal elements that make up organic compounds and give the number of bonds each typically forms.

3. Why are the following molecular formulas impossible?

CH6, C3H3, C3H9

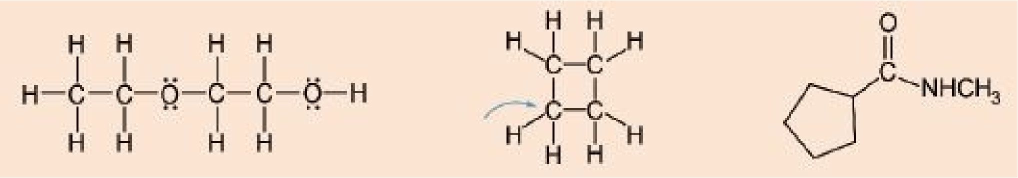
4. Which molecular formulas represent organic compounds and which represent inorganic compounds?

C3H6, H2SO4, SO2, CO, H2CO3

5. Draw in all hydrogens and lone pairs in each compound.

- C-C-C-
- C-C=O
- C-N-C-

6. Convert each compound to a condensed formula.



Terminology

- derivative - туынды / производное
- hydrocarbons - көмірсутектер /углеводороды
- adhesives - желімдер / клеи
- established - орнатылған / установленный

12.2 HOMOLOGOUS SERIES AND FUNCTIONAL GROUPS OF ORGANIC COMPOUNDS

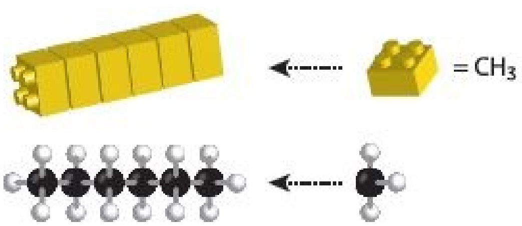
Why each compound need to have its own name?

You will:

- explain the formation of homological series and the similarity of the properties of their homologues;
- draw structural formulas of compounds and name them using IUPAC nomenclature.

Homologous series

Hydrocarbons are organic compounds that contain the elements carbon and hydrogen only. The alkanes have the general formula CnH2n+2 where n, the number of carbon atoms, such as 1, 2, 3, 4, 5 and so on. A family of compounds whose formulae differ by – CH2 is called a homologous series.



Homologous alkane chains

IUPAC nomenclature of organic compounds

There are millions of organic compounds and to name each of them IUPAC (International Union of Pure and Applied Chemistry) system is used. According to the IUPAC system, there is only one name for a compound.

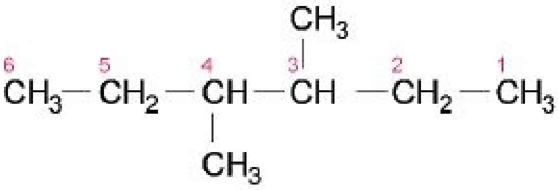
To name the alkanes, simplest members of organic chemistry, according to the IUPAC system the following rules can be used.

1. Determine the chain with the longest continuous number of carbon atoms. This gives the starting name (often called the parent name) of the alkane.

There are six carbon atoms in the longest chain in the example. So the parent name of the compound is hexane

2. Number the carbon atoms in the longest chain, starting at the end closest to the branching.

When two or more different substituents are bonded to the carbon chain, they ordered



3,4-dimethylhexane

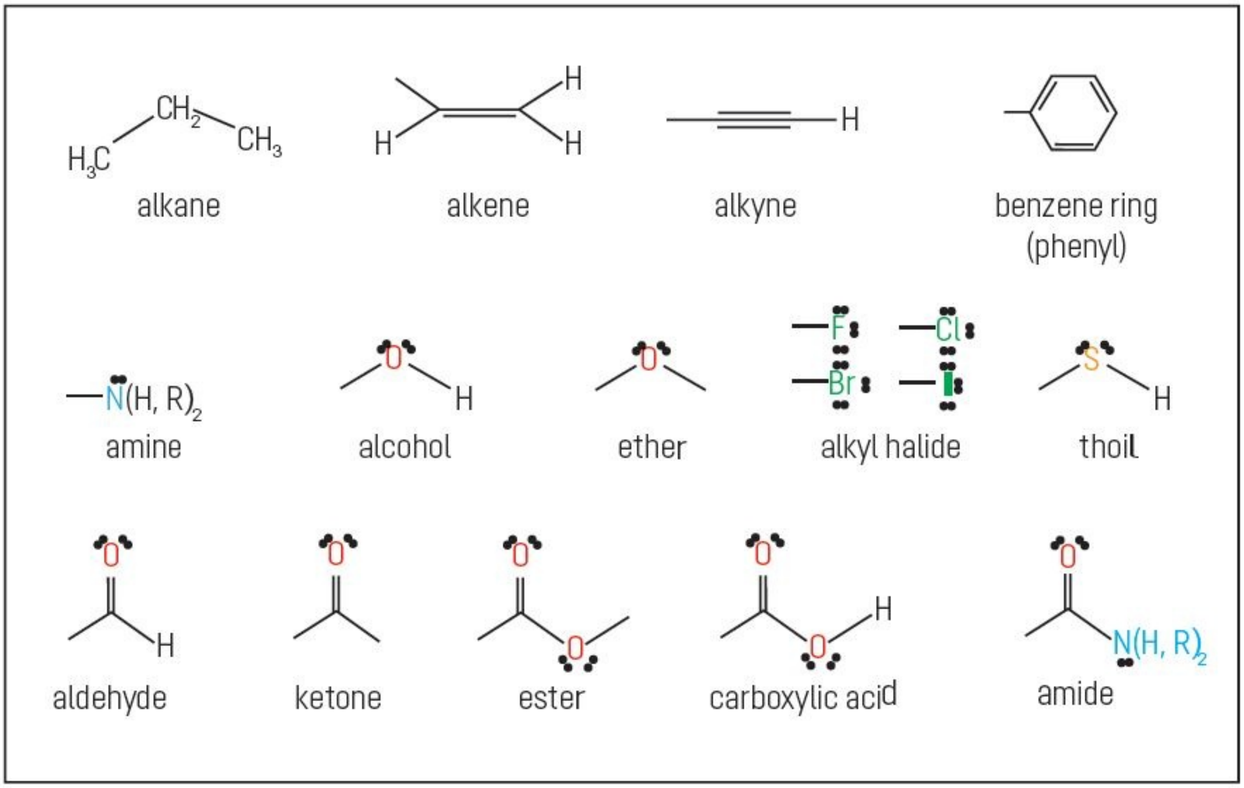
Functional groups

Organic compounds differ in their abundance and variety. Therefore, their systematization is necessary. Organic compounds are classified, taking into account two basic structural features: structure of the carbon chain (carbon skeleton) and presence and structure of functional groups.

Carbon skeleton (carbon chain) - a sequence of chemically bonded carbon atoms.

Functional group - atom or group of atoms, determining the belonging of a compound to a certain class and responsible for its chemical properties.

The compounds, which include only carbon and hydrogen, are called hydrocarbons. Other, more numerous, organic compounds can be considered as derivatives of hydrocarbons, which are formed when hydrocarbons are introduced into functional groups containing other elements. Depending on the nature of the functional groups, organic compounds are divided into classes. Some of the most characteristic functional groups and their corresponding classes of compounds are listed in the table.



Functional Groups

Literacy

1. A compound is composed of 81.8% C and 18.2% H by mass.

- - What is the empirical formula of the compound?
- - If the molecular mass of the compound is 44, what is the molecular formula of the compound?

2. A liquid compound is found to be 52.1% C and 13.1% H. What is the molecular formula of the compound?

3. Name the following compounds:

- - CH3-CH2-CH2-C(CH3)3
- - CH3-CH(CH3)-CH2-CH2-CH3
- - CH3-C(CH3)2-CH2-C(CH3)2-CH3
- - CH3-CH2-CH2-CH2-CH2-CH2-CH2-CH3
- - CH3-CH2-CH2-C(C2H5)2-CH2-CH2-C(CH3)3

4. Which of the following molecular formulas have the same empirical formula?

- - C6H12O6
- - C3H6O3
- - C12H22O11
- - C2H6O
- - C2H4O
- - C6H6
- - C2H2
- - C10H10
- - C2H6

Terminology

- homologous series - гомологтық қатарлар / гомологический ряды
- functional group - функционалды топ / функциональная группа
- IUPAC nomenclature - ИЮПАК номенклатурасы /

номенклатура ИЮПАК

12.3 ISOMERISM

Glucose and fructose have the same formula but don't function the same, why? Why does glucose have a higher normal boiling point than fructose when they have the same molecular formula?

You will:

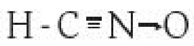
- name isomerism types and formulate isomer formulas: structural, bond position, functional groups and interclass;
- construct models of organic compounds.

Isomerism

Before the theory of structure, substances of the same elemental composition, but with different properties, were known. Such substances were called isomers, and the very phenomenon is called isomerism. Isomers are compounds with the same molecular formulas but different structures. (Isomer from Greek, isomeres; isos = "equal", meros = "part".)

The phenomenon of isomerism was discovered in 1824 independently of each other by Justus Liebig and Friedrich Wöhler. Through research, they found that there are two substances of the same composition, but with different properties:

Cyanic acid



Fulminic acid

There are two main types of isomerism in organic chemistry:

Structural isomerism and Stereoisomerism.

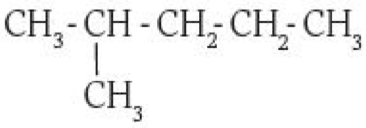
Structural isomerism, caused by different mutual arrangement of atoms in molecules. The following types of structural isomerism are distinguished: chain isomerism (isomerism of the carbon skeleton), position isomerism, functional group isomerism and interclass isomerism (isomerism of various classes of organic compounds).

1. Chain isomerism

Chain isomerism is due to the different order of the bond between the carbon atoms that form the skeleton of the molecule. Compounds have same molecular formula but different arrangement of carbon atoms.

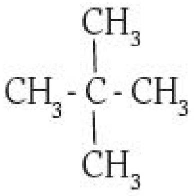
$CH_3-CH_2-CH_2-CH_2-CH_3$

n-pentane



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

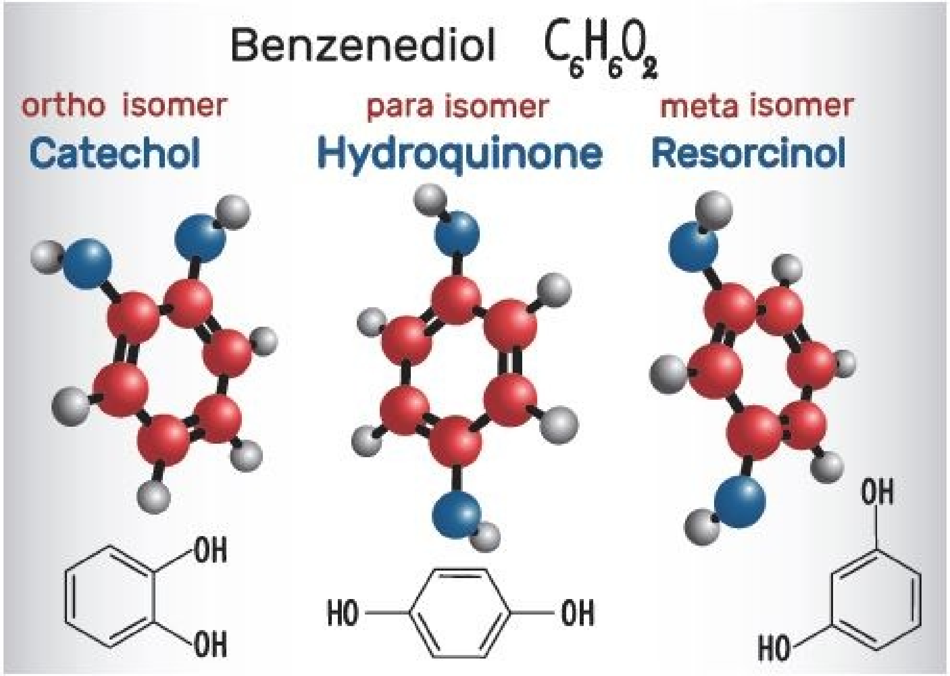
2-methylpentane



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

2,2-dimethylpropane

All isomers of pentane have the same molecular formula C5H12.



Isomers of benzenediol

2. Position isomerism

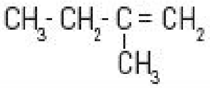
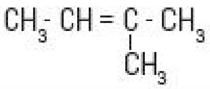
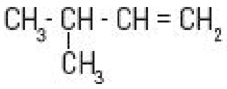
Position isomerism is due to the different position of unsaturated bond (double bond or triple bond) with the same carbon skeleton of the molecule.

$CH_2 = CH - CH_2 - CH_3$ C_4H_8 (1-butene)

$CH_3 - CH = CH - CH_3$ C_4H_8 (2-butene)

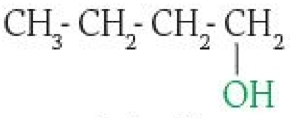
The only difference between 1–butene and 2–butene is the location of C=C double bond.

Table 18 *Some isomers of pentene. Position isomerism*

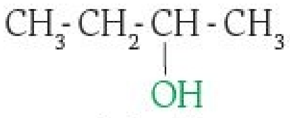
Name	Molecular formula	Structural formula	Boiling point, °C
1-pentene	C_5H_{10}	$CH_3-CH_2-CH_2-CH=CH_2$	30
2-pentene	C_5H_{10}	$CH_3-CH_2-CH=CH-CH_3$	36.5
2-methyl-1-butene	C_5H_{10}	 $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{C}}=CH_2$	31.3
2-methyl-2-butene	C_5H_{10}	 $CH_3-CH=\underset{\displaystyle CH_3}{\underset{\vert}{C}}-CH_3$	38.5
3-methyl-1-butene	C_5H_{10}	 $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH=CH_2$	20.15

3. Functional group isomerism

Functional group isomerism is due to the different position of functional group with the same carbon skeleton of the molecule.


$CH_3-CH_2-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}}$

butanol-1


$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

butanol-2

The only difference between butanol-1 and butanol-2 is the location of -OH hydroxyl group.

4. Interclass isomerism

Interclass isomerism is due to different positions and combinations of atoms in molecules of substances having the same molecular formula, but belonging to different classes.

CH_3-CH_2-OH

ethyl alcohol

CH_3-O-CH_3

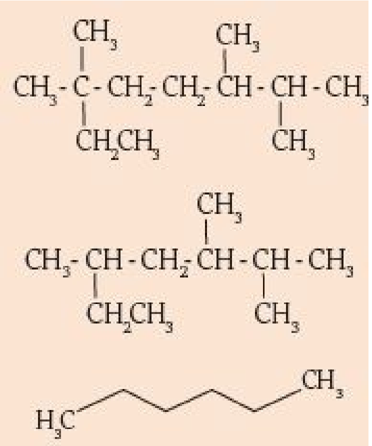
dimethyl ether

Ethyl alcohol and dimethyl ether have the same molecular formula C2H6O.

Literacy

1. Draw and name the isomers of C5H12

2. Name the following:



3. Draw all the structural isomers of C6H14.

4. Draw all the structural isomers of C3H7Cl.

5. Draw the cis and trans isomers of each compound:

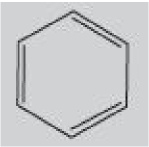
- \- C(CH3)2=CH-CH3
- -C(CH3C2H5)=CH-CH3

6. Draw condensed formulas for the following compounds:

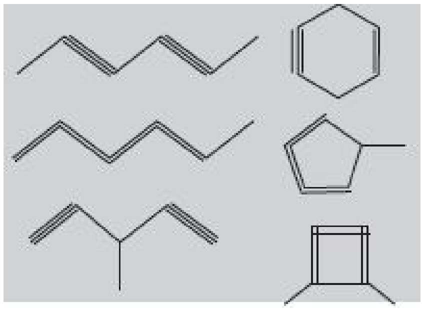
- \- 2,2,3,4-tetraethyl-pentane
- \- 2,4-diethyl-3-ethyl-hexane
- \- 2,2,3,3,4,4-hexamethylhexane

Chemfact

German chemist Friedrich Kekule was found the correct structural formula for benzene C6H6.



Some possible structures of benzene were found before Kekula. But they were wrong. Some benzene structures are given below:

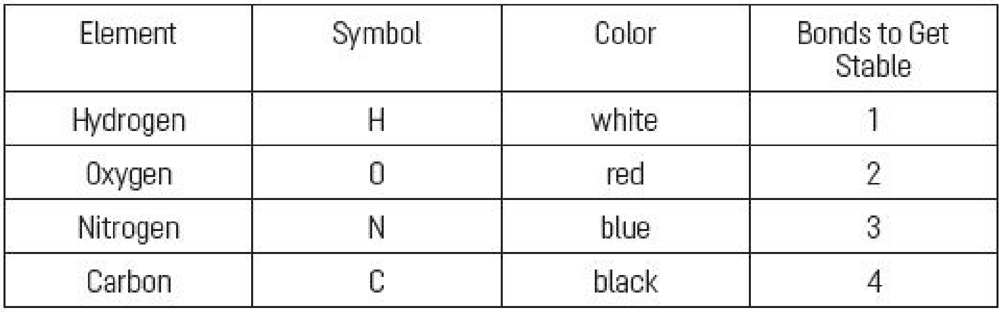


Lab work №4

Molecular models of organic compounds

Use the following information to create your lab report in the classwork section of your notebook. Include the following sections.

Molecular models



Element	Symbol	Color	Bonds to Get Stable
Hydrogen	H	white	1
Oxygen	O	red	2
Nitrogen	N	blue	3
Carbon	C	black	4

Terminology

- isomers - изомерлер / изомеры
- fulminic acid - фульмин қышқылы / фульминовая кислота
- stereoisomers - стереоизомерлер / стереоизомеры
- cis-trans isomers - цис-транс изомерлер / цис-транс изомеры.

12.4 ALKANES. CHEMICAL PROPERTIES OF ALKANES

Titan (Saturn's satellite) contains methane (1.6%) in liquid form, there are methane lakes (mixture with ethane) and methane rains on Titan. Why does methane exist in liquid form on the Titan?

You will:

- study the combustion of various alkanes and explain their use as a fuel;
- evaluate combustion products of alkanes and their ecological impact on environment;
- determine the molecular formula of the substance according to the combustion products;
- explain the free radical mechanism of the substitution reaction on the example of alkane halogenation.

Alkanes

Saturated hydrocarbons find wide application in the most diverse spheres of life and human activity. Gaseous alkanes (methane and propane-butane mixture) are used as a valuable fuel. Liquid hydrocarbons make up a significant share in motor and rocket fuels and are used as solvents.

Biogas for animal waste

Combustion reactions

Alkanes produce CO_2 and H_2O when they are burnt. In these reactions, a large amount of energy is released. For this reason, natural gas, which contains a mixture of alkanes, is a useful fuel. The general formula for a combustion reaction is

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$, $\Delta H^o = -890$ kJ/mol

$C_4H_{10}(g) + 6.5O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$, $\Delta H^o = -2875.8$ kJ/mol

$C_nH_{2n+2} + (3n+1)/2O_2(g) \rightarrow nCO_2(g) + (n+1)H_2O(l)$, $\Delta H^o = -890$ kJ/mol

Due to the evolution of large amount of heat during combustion, alkanes are used as fuels. During incomplete combustion of alkanes with insufficient amount of air or oxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.

$CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(l)$ (incomplete combustion)

$CH_4(g) + 1.5O_2(g) \rightarrow CO(g) + 2H_2O(l)$

Gas burner

Manual gas burner with blue flame

Big biogas plant

Ecological impact of burning of alkanes

One of the main sources of environmental pollution is the burning of hydrocarbons. People burn them in form of coal, natural gas and petroleum products. Incomplete burning of hydrocarbons leads to formation of carbon monoxide gases, in which 65% of all emissions are transport, 21% - for small consumers and household sector, and 14% - for industry. Carbon monoxide is the most dangerous and widespread of gaseous air pollutants. It is dangerous because it combines with hemoglobin of the blood, resulting in the formation of carboxyhemoglobin. An increase in the level of carboxyhemoglobin in the blood can cause disruption of the functions of the central nervous system: vision, reaction, orientation in time and space weakens.

This kind of pollution is especially dangerous for patients with cardiovascular diseases.

Burning of natural alkanes

Substitution reactions

In this type of reaction, an atom in a molecule is replaced with another atom or group. Alkanes may undergo substitution reactions with halogens and nitric acid. The first reactions are often called halogenation and the second nitration reactions. In halogenation reactions, chlorine and bromine are generally used, since fluorine reacts very rapidly and produces a large amount of energy and iodine does not undergo substitution reactions. The general representation of a substitution reaction is:

$$\underset{\text{Alkane}}{R-H} + \underset{\text{Halogen}}{X-X} \xrightarrow{h\nu,\ \text{heat}} \underset{\text{Alkyl halide}}{R-H} + HX$$

When a large amount of heat and light is used, radicals of Cl and CH4 are formed and the reaction occurs in a series of steps.

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Dichloromethane}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Trichloromethane}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Tetrachloromethane}}{CCl_4} + HCl$$

It is found that the rate of reaction of alkanes with halogens is

F2 > Cl2 > Br2 > I2.

Mechanism

Initiation: The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl–Cl bond is weaker than the C–C and C–H bond and hence, is easiest to break

$$\mathrm{Cl - Cl} \xrightarrow{h\nu,\ \text{homolysis}} \underset{\text{Chlorine free radicals}}{\mathrm{Cl}\bullet + \bullet\mathrm{Cl}}$$

Propagation: Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl.

$$\mathrm{CH_4 + Cl\bullet} \xrightarrow{h\nu} \mathrm{CH_3\bullet + H - Cl}$$

The methyl radical thus obtained attacks the second molecule of chlorine to form CH3–Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule.

$$\mathrm{CH_3\bullet + Cl\text{-}Cl} \xrightarrow{h\nu} \mathrm{CH_3\text{-}Cl + Cl\bullet}$$

The chlorine and methyl free radicals generated above repeat steps (a) and (b) respectively and thereby setup a chain of reactions. The propagation steps (a) and (b) are those which directly give principal products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly haloginated products are formed.

$$\mathrm{CH_3Cl + Cl\bullet \rightarrow \bullet CH_2\text{-}Cl + HCl}$$
$$\mathrm{\bullet CH_2\text{-}Cl + Cl\text{-}Cl \rightarrow CH_2Cl_2 + Cl\bullet}$$

Termination: The reaction stops after some time due to consumption of reactants and / or due to the following side reactions : The possible chain terminating steps are :

(a) $Cl\bullet + Cl\bullet \rightarrow Cl - Cl$

(b) $\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$

(c) $\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$

Though in (c), $CH_3 – Cl$, the one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane.

Example 1

Determination of empirical and molecular formula of alkanes

When 2.2 g of an alkane is burnt completely 3.36 L of CO_2 is produced at STP. What is the molecular formula of this alkane?

Solution

The general equation for the combustion of alkanes is

$$C_nH_{2n+2} + ((3n+1)/2)O_2 \rightarrow nCO_2 + (n+1)H_2O$$

Step1

Let us find the number of moles in 3.36 L of CO_2 at STP:

$$n(CO_2) = V(CO_2) / V_{STP} = 3.36\ L / 22.4\ L/mol = 0.15\ mol\ CO_2$$

Step2

We can now find the number of moles of alkane as:

1 mol alkane ------ n mol CO_2

x mol alkane ------ 0.15 mol CO_2

$x = (1 \text{ mol} \times 0.15 \text{ mol}) / n \text{ mol} = 0.15/n$

Molar mass of alkane: $Mr(C_nH_{2n+2}) = 12n + 2n + 2 = 14n + 2$

Step3

Moles of alkane

n(alkane) = m(alkane) / Mr(alkane)

$0.15 / n = 2.2 / (14n+2)$

$2.2n = 2.1n + 0.3$

$0.1n = 0.3$ $n = 3$

The formula of alkane is C_3H_8 - propane

Example 2

A 1.50 g sample of alkane undergoes complete combustion to produce 4.40 g of CO_2 and 2.70 g of H_2O. What is the empirical formula of unknown alkane?

Solution

Step 1

Determine the grams of carbon in 4.40 g CO_2 and the grams of hydrogen in 2.70 g H_2O:

$m(C) = 1 \times Ar(C) \times [m(CO_2) / Mr(CO_2)] = 12 \times (4.4 / 44) = 1.2$ g of C

$m(H) = 2 \times Ar(H) \times [m(H_2O) / Mr(H_2O)] = 2 \times 1 \times (2.7 / 18) = 0.3$ g of C

Step 2

Convert grams of C and H to their respective amount of moles:

$n(C) = m(C) / Ar(C) = 1.2 / 12 = 0.1$ mol of C

$n(H) = m(H) / Ar(H) = 0.3 / 1 = 0.3$ mol of H

Step 3

Divide each molar amount by the lowest value, seeking to modify the above molar amounts into small, whole numbers

C: 0.1 mol / 0.1 mol = 1

H: 0.3 mol / 0.1 mol = 3

The empirical formula of alkane is CH_3

Literacy

1. When 21 g of an alkane is burnt completely 31.36 L of CO_2 is produced at STP. What is the molecular formula of this alkane?

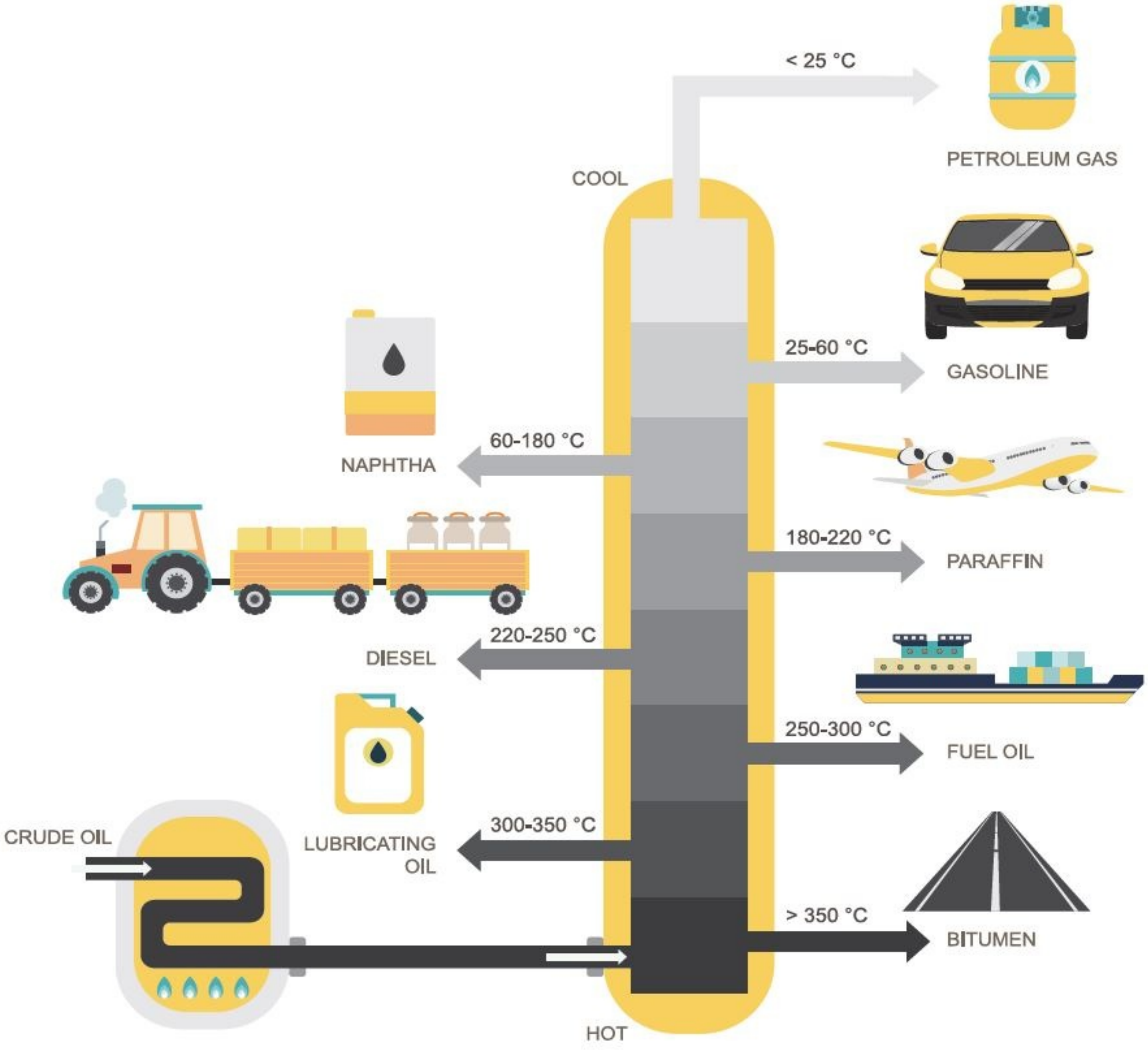
2. When 18.56 g of an alkane is burnt completely 56.32 g of CO_2 and 28.8 g of water is produced. What is the molecular formula of this alkane?

3. A 26.4 g sample of alkane undergoes complete combustion to produce 79.2 g of CO2 and 43.2 g of H2O. What is the empirical formula of unknown alkane?

4. A storage tank (40 m3) contains a mixture of hydrocarbons: 60% of CH4, 35% of C2H6, 5% of C3H8 burnt completely. Find volume of CO2 gas after combustion.

Chemistry around us

Fractional distillation is a special type of distillation designed to separate a mixture of two or more liquids that have different boiling points.



Fractional distillation of crude oil

Literacy

1. How many double bonds in benzene molecule?
2. What is benzene? Who discovered its stable structure?
3. Where is used benzene derivatives?
4. What volume of oxygen is needed to burn 56 liters of benzene at STP?
5. Find the mass of benzene that is obtained from the acetylene

that takes up a volume of 13.44 L at STP. The yield of the reaction is 80%.

Terminology

- halogenation - галегендеу /галогенирование
- satellite - серік / спутник
- initiation - инициация
- propagation - таралу /распространение
- termination - аяқталу, тоқтау/ прекращение

12.5 CYCLOALKANES

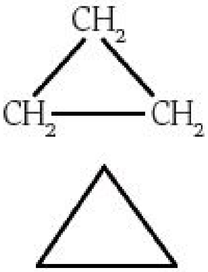
Why is the general formula of alkene and cycloalkane the same?

You will:

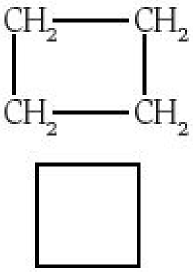
- know the homologous series, structure, chemical and physical properties of cycloalkanes.

Nomenclature of cycloalkanes

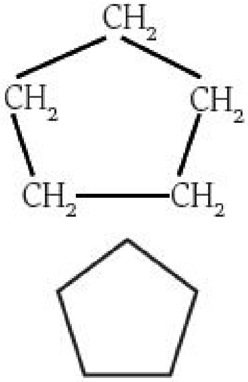
Cycloalkanes are named by adding the prefix cyclo – to the names of the alkanes. For example, the cycloalkane with three carbon atoms is called cyclopropane.



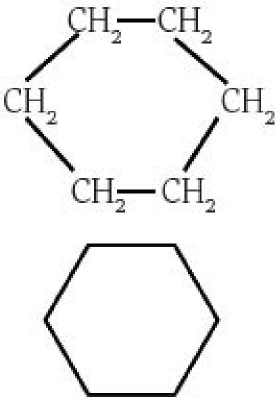
C_3H_6
cyclopropane



C_4H_8
cyclobutane



C_5H_{10}
cyclopentane



C_6H_{12}
cyclohexane

If there is a substituent attached to the ring, we name them as, alkylcycloalkanes, halocycloalkanes, etc.

Physical properties

The melting points, boiling points and densities of cycloalkanes are different from the alkanes possessing the same number of carbon atoms. For example; the melting point of heptane is –90.5°C, the boiling point is 98.4°C and the density is 0.684 g/mL; whereas for cycloheptane these values are –12°C, 118.5°C and 0.808 g/mL respectively.

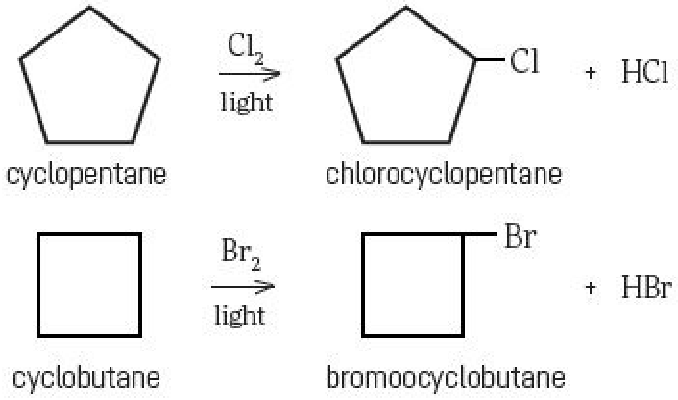
Table 19 *The first five cycloalkanes and some of their physical properties*

Chemical name	Molecular formula	Density	Melting point, °C	Boiling point, °C
Cyclopropane	C_3H_6	1.809	-127	-33
Cyclobutane	C_4H_8	0.703	-80	+13.1
Cyclopentane	C_5H_{10}	0.746	-94.4	+49.3
Cyclohexane	C_6H_{12}	0.778	+6.47	+80.7
Cycloheptane	C_7H_{14}	0.809	-12	+118.5

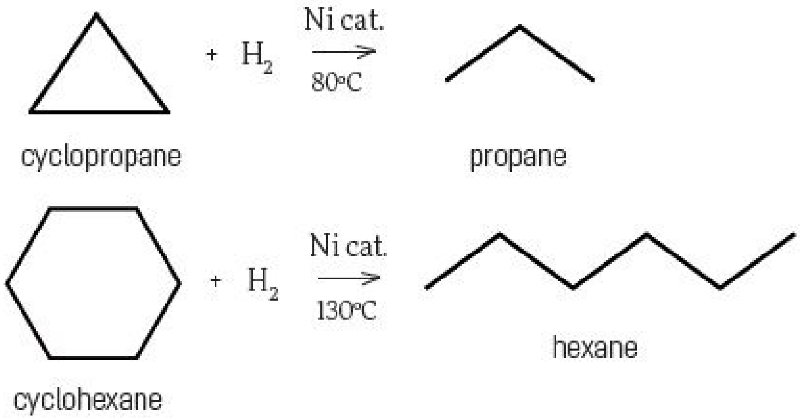
Chemical properties

The chemical properties of cycloalkanes show some differences from those of alkanes.

1. Cycloalkanes that have more than five carbon atoms undergo substitution reactions. In the substitution reactions of alkanes there can be more than one product, but in cycloalkanes, there can only be a single product.

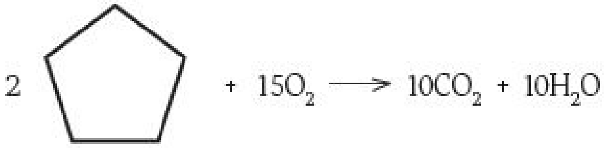


2. Cycloalkanes which have four or three carbon atoms undergo addition (hydrogenation) reactions with a catalyst.



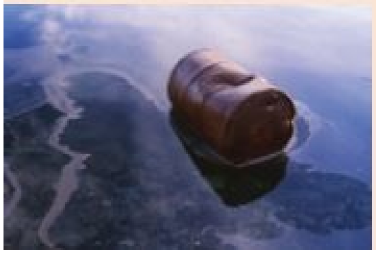
The cycloalkane having bigger ring strain undergoes the reaction more easily.

3. Complete combustion of cycloalkanes produces carbon dioxide gas and water vapor.



Chemistry around us

Many cycloalkanes are used in motor fuel, natural gas, petroleum gas, kerosene, diesel, and many other heavy oils.



Chemfact

The most common and useful cycloalkanes in organic chemistry are cyclopentane and cyclohexane.

Literacy

1. Draw the structural formulas of cycloheptane and cyclooctane.

2. Write the chemical reactions of cyclobutane with H_2 and Cl_2 gases.

3. Why cycloalkanes are insoluble in water?

4. Find molecular formula of cycloalkane if relative density of unknown cycloalkane according to hydrogen is 42.

5. A compound gave an analysis of the following percentage composition: C=85.71%, H=14.29%. Derive the empirical formula of the compound.

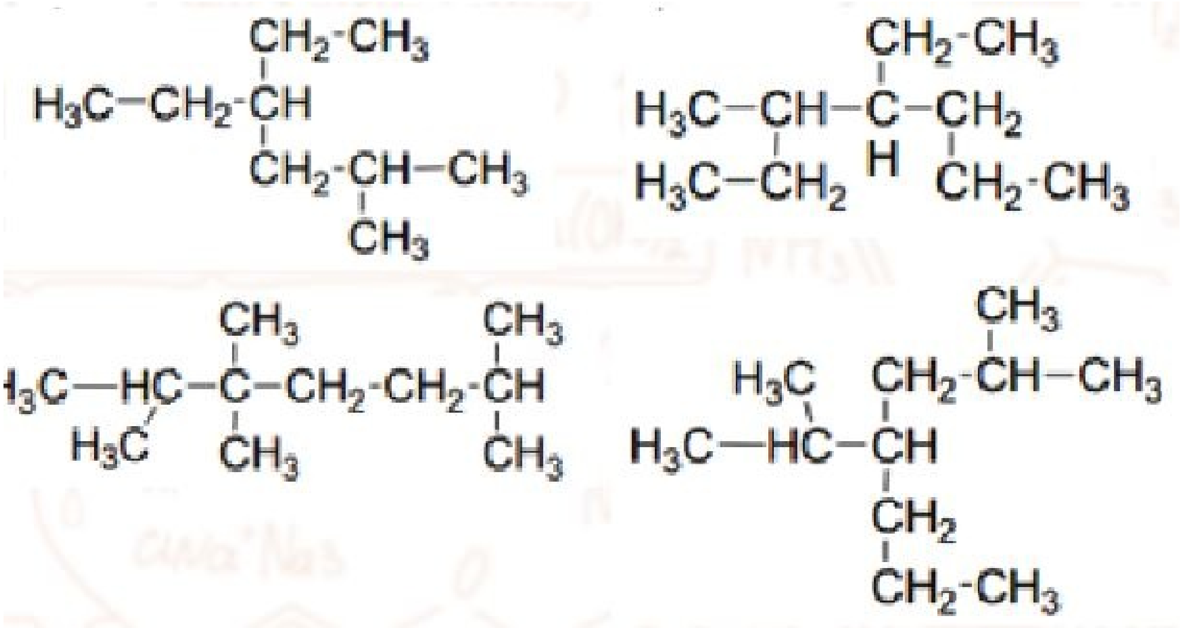
QUESTIONS AND PROBLEMS

1. Draw structures that have different atom arrangements for hydrocarbons with:

- - Five C atoms, no multiple bonds and no rings
- - Three C atoms, one double bond and no rings

Alkanes

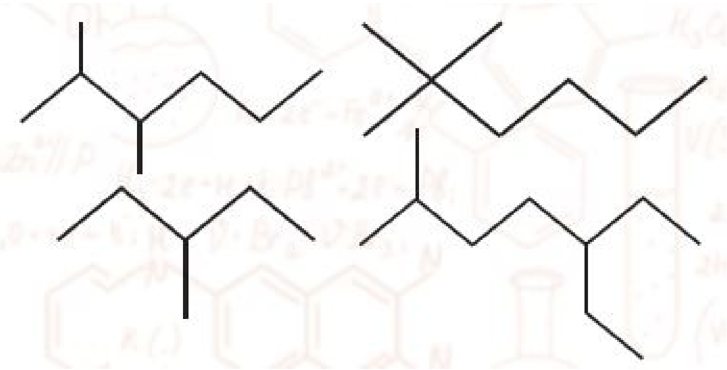
1. Give the systematic name for each of the following:



2. Draw condensed formulas for the following compounds:

- - 2,2,3,4-tetraethyl-pentane
- - 2,4-diethyl-3-ethyl-hexane
- - 2,2,3,3,4,4-hexamethyl-hexane
- - 2,3,6-trimethyl-3-ethyl-heptane

3. Suggest IUPAC name for each of the following hydrocarbons:



4. Define a functional group. Name some such group containing an oxygen atom.

5. Write structures and names for all the isomers of the alkane of formula C5H12.

6. A mixture of ethyl- and propyl iodides is heated with metallic sodium. Predict the products.

7. What is the cracking process? When in the process of cracking what other molecules are produced from this reaction?

8. Write the major products of each of the following reactions:

- - C3H6 + H2 →
- - C3H8 + 2Cl2 →
- - C2H5Cl + CH3I + Na →
- - C3H8 + O2 →
- - C8H18 (cracking) →

9. A sample of gaseous hydrocarbon occupying 4.48 liters at STP when completely burnt in air produced 17.6 g of CO2 and 10.8 g of H2O. Calculate the molecular mass and mass of the compound and the volume of oxygen at STP, required for its burning.

10. 57.6 g of alkane when completely burnt in air produced 176 g of CO2 and 86.4 g of H2O. Calculate the molecular mass and mass of the alkane and the volume of oxygen at STP, required for its burning.

11. A 121.8 g sample of an alkane was combusted in a oxygen to yield 369.6 g CO2 and 189 g H2O. Relative density of this alkane according to air is 2.0. What is its molecular formula?

12. What are the main differences between the structures of propene and propane?

13. What is the difference between fractional distillation and catalytic cracking?

14. Describe process of fractional distillation.

15. What are the products produced from the fractional distillation of oil?

16. Why is refined oil more hazardous to the marine environment than crude oil?

17. What are some waste products of petroleum and how can they affect the environment?

18. What can be produced from natural gas? How is natural gas drilled?

Empirical and molecular formulas

1. A compound gave a analysis the following percentage composition: C=82.76%, H=17.24%. Derive the molecular formula of the compound.

2. A compound gave a analysis the following percentage composition: C=81.82%, H=18.18%. Derive the molecular formula of the compound.

3. Derive the empirical formula of a compound that on analysis gave the following percentage composition: C=60.00%, H=13.33%, O=26.67%.

4. A compound gave an analysis of the following percentage composition: C=40.00%, H=6.67%, O=53.33%. Derive the empirical formula of the compound.

5. Derive the molecular formula of a compound that on analysis gave the following percentage composition: C=26.67%, H=2.22%, O=71.11%. Molecular mass of a compound is 90 g/mol.

13
CHAPTER

UNSATURATED HYDROCARBONS

CHAPTER 13: UNSATURATED HYDROCARBONS

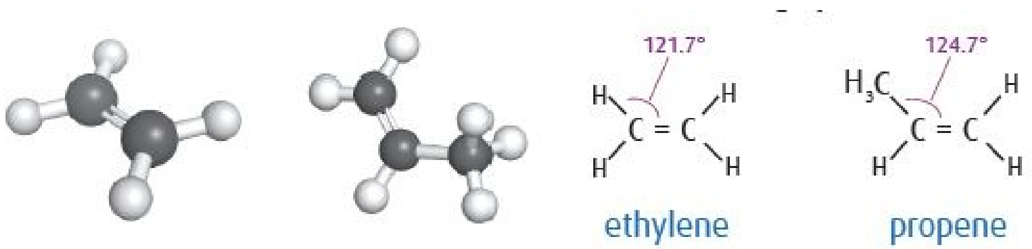
13.1 ALKENES

Why is chlorophyll green? Why does phenolphthalein indicator change from colorless to pink in a pH above of 8.2?

You will:

- explain the term"unsaturated" and the effects of unsaturation on the properties of the compound;
- demonstrate that alkenes are unsaturated.

Alkenes is another type of hydrocarbons though this group of compounds is an unsaturated. Alkenes contain carbon-carbon double bond that give them ability to add more hydrogens to their structure. The general formula of alkenes is CnH2n, where n - any number starting with 2. The very first member of alkenes is an ethene, C2H4.



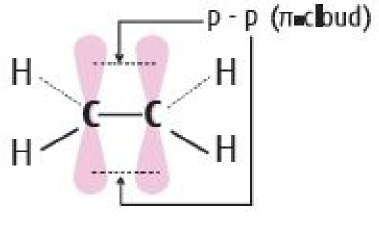
ethylene

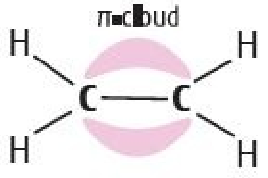
propene

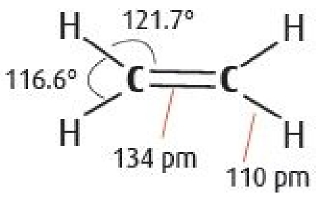
First four members of alkenes are gases at room temperature. Alkenes which contain from 5 to 17 carbon atoms are liquids, and the rest are solids.

Structure of Double Bond

Double bond between two carbons in alkenes consists of one strong sigma bond and one weak pi (π) bond. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm). The energy formation for sigma bond is about 397 kJ/mol while that for pi (π) bond is 284 kJ/mol, so the presence of the pi (π) bond makes alkenes ready for undergoing addition reactions.







Nomenclature

The IUPAC rules for naming alkenes:

1) Name the longest chain that contains the double bond. The characteristic name ending is -ene.

2) Number the longest chain of carbon atoms so that the carbon atoms joined by the double bond have numbers as low as possible.

3) Locate the double bond by the lower-numbered carbon atom bound by the double bond.

4) Locate and name attached groups.

5) Combine the names for the attached groups and the longest chain into the name.

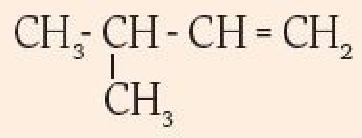
Carotene $C_{40}H_{56}$ is polyene occurring in carrot. Carotenes are polyunsaturated hydrocarbons

Table 20 *Physical properties of alkenes*

IUPAC name	*Structural formula*	*Boiling point (°C)*	*Melting point (°C)*	*Density g/ml*
ethylene	$CH_2=CH_2$	-104	-169	0.38
propene	$CH_2=CH-CH_3$	-47	-185	0.52
butene-1	$CH_2=CH-CH_2-CH_3$	-6	-185	0.60
pentene-1	$CH_2=CH-CH_2-CH_2-CH_3$	30	-138	0.64
hexene-1	$CH_2=CH-CH_2-CH_2-CH_2-CH_3$	63	-140	0.67

Example 1

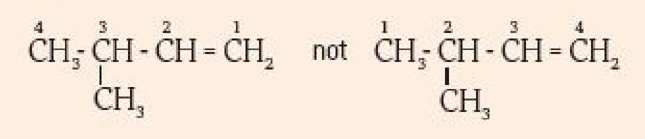
Name the following alkene.



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}-CH=CH_2}$$

Solution:

To give lower numbers to the carbons bound by the double bond, the chain is numbered from the right:



$\overset{4}{C}H_3-\underset{CH_3}{\underset{|}{\overset{3}{C}H}}-\overset{2}{C}H=\overset{1}{C}H_2$ not $\overset{1}{C}H_3-\underset{CH_3}{\underset{|}{\overset{2}{C}H}}-\overset{3}{C}H=\overset{4}{C}H_2$

Thus, the compound is a butene-1 with an attached methyl group on carbon 3. Therefore, the name is 3-methyl-butene-1

Example 2

Calculate number of sigma (σ) and pi (π) bonds in the below structures:

a) butene-1

b) 2-methylpenene-1

c)2-methylbutene-2

Solution:

a) σ bonds: 11, π bond: 1

b) σ bonds: 17, π bond: 1

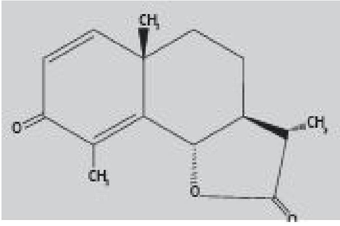
c) σ bonds: 14, π bond: 1

Chemfact

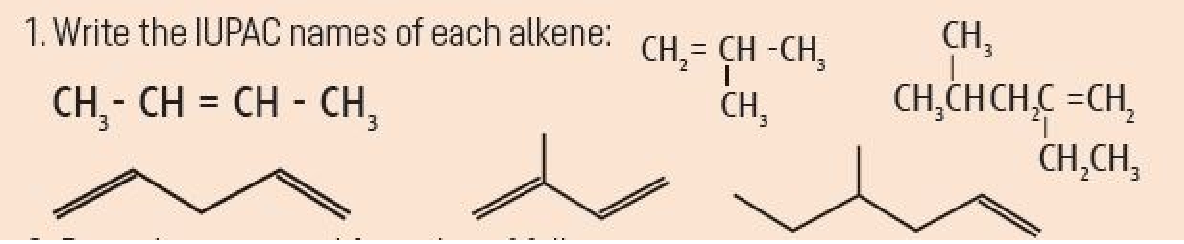
Good food source of lycopene is tomatoes. Lycopene C40H56 is unsaturated organic compound

Chemfact

Santonin, isolated from the bloom heads of certain species of Artemisia. Santonin is natural polyene with has strong antiseptic properties and used in medicine. Artemisia plant widely distributed in Kazakhstan



Literacy



1. Write the IUPAC names of each alkene:

$CH_3-CH=CH-CH_3$

$CH_2=CH(CH_3)-CH_3$

$CH_3CH(CH_3)CH_2C(CH_2CH_3)=CH_2$

2. Draw the structural formulas of followings

- \- Cl-CH=CH-Cl

- - $CH_2=CH-Cl$
- - $CH_3-CH=CH-CH_3$

3. Draw the structural formulas of followings

- - 3-methyl-butene-1
- - 2-ethyl-pentene-1
- - 4-ethyl-3,3-dimetyl-octene-1
- - 2-methyl-butene-2

Terminology

- unsaturated - қанықпаған /ненасыщенный
- overlapping - жабылатын /перекрытие
- lateral - жанынан / боковая
- lycopene - ликопин /ликопин
- carotene - каротин / каротин
- santonin - сантонин /сантонин

Lab work №5

QUALITATIVE ANALYSIS OF UNSATURATED HYDROCARBONS

Hydrocarbon molecules that contain a double bond are called as alkenes. The two carbon atoms linked by a double bond, one σ (sigma) bond and one π bond. Ethene (Ethylene), C_2H_4, is the simplest alkene. Each carbon atom in ethylene has a trigonal planar structure. The bond angles at each carbon are approximately 120°. Each carbon atom is attached to only three atoms by sigma bonds. The unhybridized 2p orbitals of carbon atoms may also overlap to form a second bond (a π bond).

Materials:

Ethanol C_2H_5OH 100 ml, sand, conc. sulfuric acid H_2SO_4 10 ml, potassium permanganate $KMnO_4$ 1-2% solution, large test tube, hole stopper, ring stand, clamp, beaker, glass tube, Bunsen burner.

Procedure:

1. Place ethanol, sand, and conc. sulfuric acid into a flask.

2. Then, make connection with stopper, glass tube into beaker containing $KMnO_4$ solution.

3. Heat the flask.

4. Replace $KMnO_4$ solution with bromine Br_2 water.

5. Ignite formed gas.

Observation:

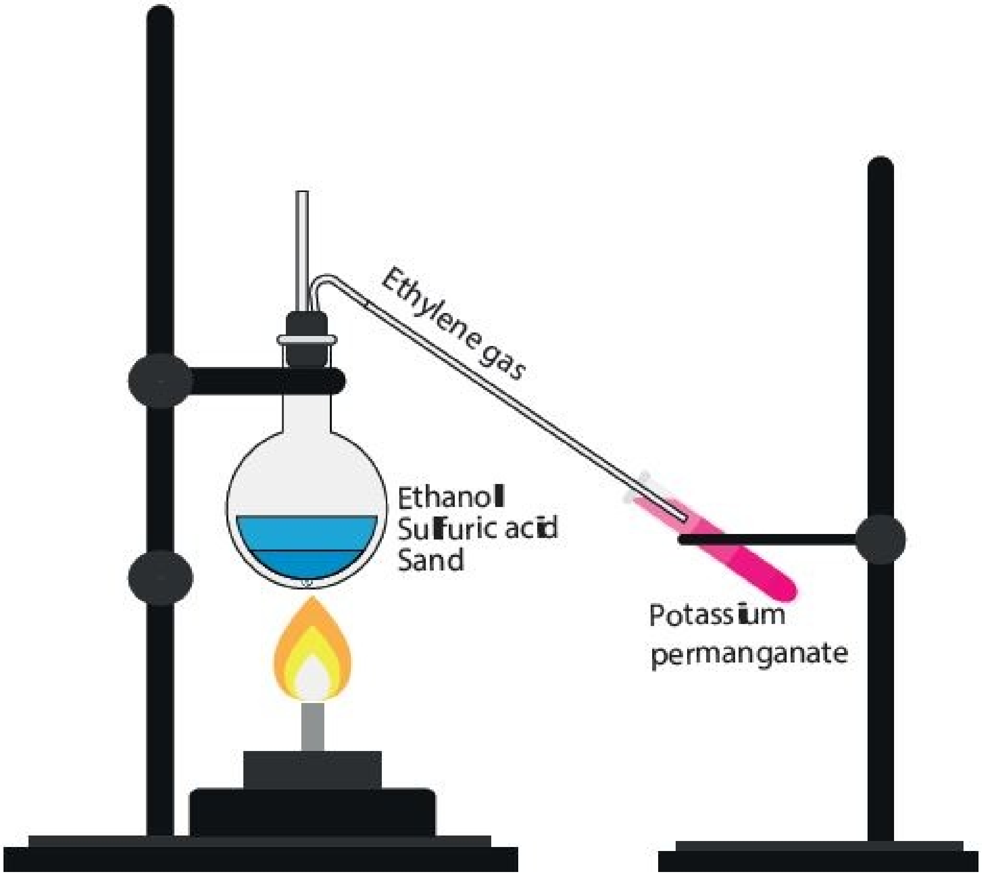
Write the preparation reaction of ethylene from ethanol.
…… .

- - The color of $KMnO_4$ solution turns into …………………………… from ……………………as a result of the formation of ethylene during the reaction.
- - Write the chemical reaction between ethylene and $KMnO_4$ solution.
- ……………………………………………………………………………………………
- - What is the importance of H_2SO_4 in this reaction?
- ……………………………………………………………………………………………
- - In two different test tubes, there are butane and ethylene gases. How can you distinguish them?

Conclusion:

Write the observed properties of the ethylene and look up the missing properties:

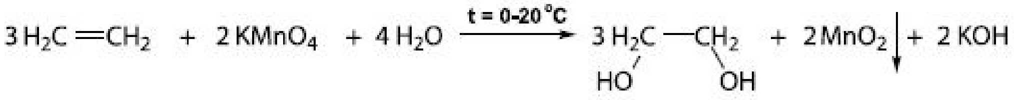
- \- Chemical formula: …………………
- \- Color: …………………
- \- Melting point: …………………
- \- Boiling point: …………………
- \- Usage: ……………………………………………………………………………



1. Decolorization of bromine solution

Ethylene 1,2-Bromoethane

2. Decolorization of potassium permanganate solution



Ethylene Ethylene glycol

13.2 STRUCTURAL AND STEREOISOMERS OF ALKENES. PREPARATION OF ALKENES

Why green fruits ripen faster in presence of ripe fruits (for example, banana and green tomato) when they are packed together?

You will:

- distinguish between cis and trans isomers and understand this as a kind of stereoisomerism;
- know the preparation reactions of alkenes.

Structural isomerism

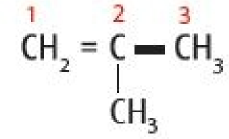
First two members of alkenes have only one structure (ethene C2H4 and propene C3H6). Alkenes with three or more carbon atoms have diff erent structures. For example, C4H6 as a molecular formula can be written in the following ways:

$\overset{1}{CH} = \overset{2}{CH} - \overset{3}{CH_2} - \overset{4}{CH_3}$

but-1-ene (C_4H_8)

$\overset{1}{CH_3} - \overset{2}{CH} = \overset{3}{CH} - \overset{4}{CH_3}$

but-2-ene (C_4H_8)



$\overset{1}{CH_2} = \underset{CH_3}{\overset{2}{C}} - \overset{3}{CH_3}$

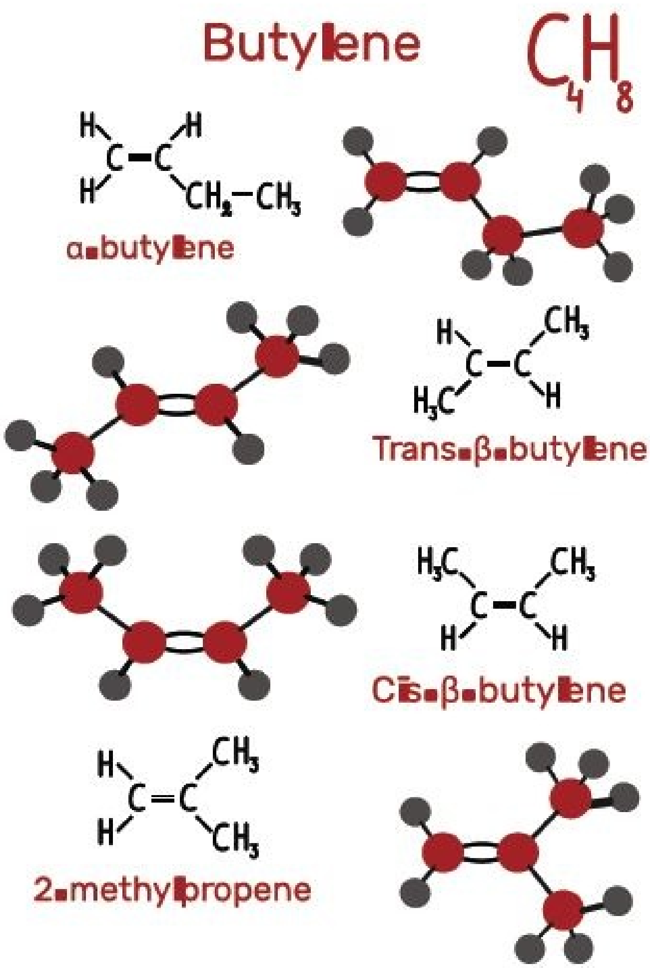
2-methylprop-1-ene (C_4H_8)

Alkenes show both structural isomerism and geometrical isomerism.

Geometrical isomerism. Cis-trans isomerism

Cis-trans isomerism is due to the different position of the substituents with respect to the double bond plane.

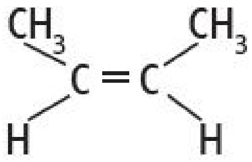
These two isomers can not be converted into one another without rotation around the double bond C = C, and this rotation requires the rupture of the π-bond and the expenditure of a large amount of energy. Therefore, cis and trans isomers are different substances that differ from one another in physical and chemical properties.

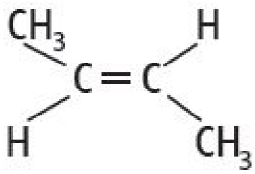


Alkenes having different double substituents on each of the two carbon atoms may exist as two space isomers, differing in the arrangement of the substituents with respect to the π-bond plane.

Thus, in the butene-2 molecule, CH3-CH=CH-CH3, the CH3 groups may be on either side of the double bond in the cis-isomer, or on opposite sides of the trans isomer.

Alkenes, in which at least one of the carbon atoms for the C = C bond has two identical substituents, do not have cis-trans isomers. For example, butene-1 CH2=CH-CH2-CH3 does not have cis and trans isomers; the first atom C is connected with two identical atoms H.





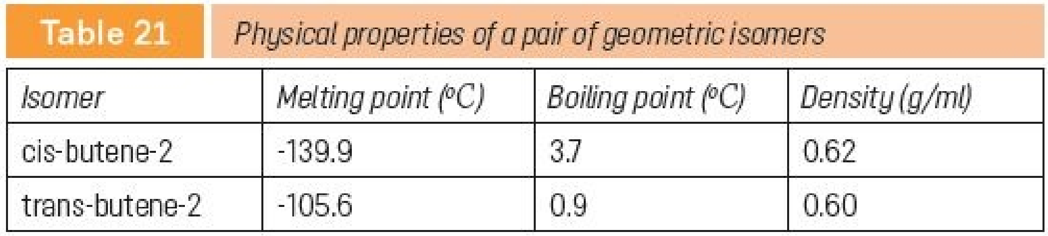


Table 21 *Physical properties of a pair of geometric isomers*

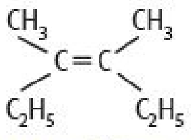
Isomer	*Melting point (ºC)*	*Boiling point (ºC)*	*Density (g/ml)*
cis-butene-2	-139.9	3.7	0.62
trans-butene-2	-105.6	0.9	0.60

Example

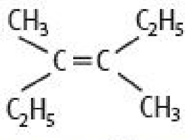
Draw cis and trans isomers of the following compound. Also write IUPAC name:

C2H5C(CH3)=C(CH3)C2H5

Solution



cis-3, 4-Dimethylhexene-3



trans-3, 4-Dimethylhexene-3

Preparation of alkenes

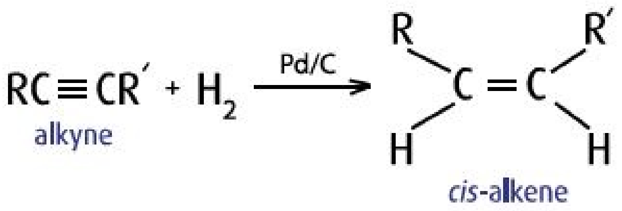
1. From alkanes

Dehydrogenation and cracking of alkanes:

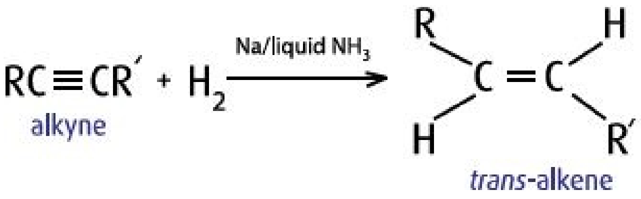
$C_{10}H_{22}$ --> C_5H_{12} + C_5H_{10} C_6H_{12} --> C_6H_{12} + H_2

2. From alkynes

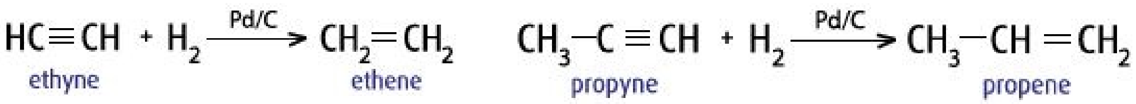
a) Alkynes react with hydrogen gas in the presence of a Pd/C catalyst:



b) Alkynes react with hydrogen in the presence of a Na/liquid NH3 catalyst:

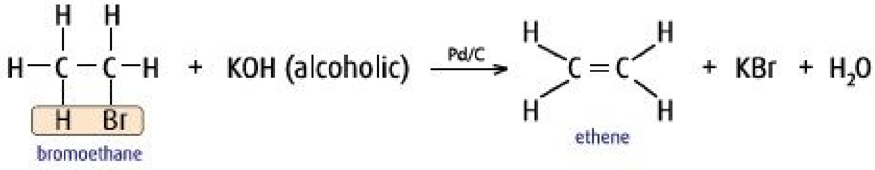


c)



3. From alkyl halides

Alkyl halides (R-X) react with alcoholic potassium hydroxide (KOH+alcohol) to give alkenes (dehydrohalogenation):

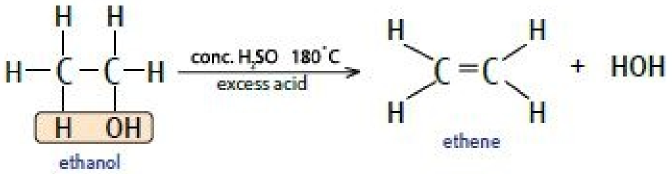


4. From dihalides (dehalogenation)

Dihalides react with zinc Zn metal to produce alkenes and zinc halide ZnX2:

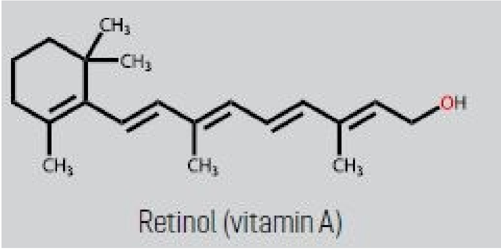
$$Zn + CH_2Br\text{-}CH_2Br \rightarrow ZnBr_2 + CH_2{=}CH_2$$

5. Alcohol reacts with concentrated sulfuric acid H2SO4 (or H3PO4, ZnCl2, Al2O3) to release alkenes and water:



Chemfact

The importance of cis-trans isomerism is observed in certain biological processes, such as vision. When light crosses the retina, a cis double bond in the compound retinal is converted to a trans double bond. The conversion starts a chain of events that finally results in our being able to see.



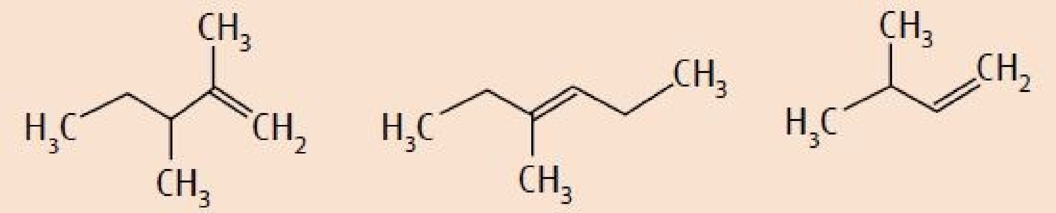
Chemfact

Vegetable oils synthesized from olives, corn are formed from unsaturated organic molecules such as oleic acid, linoleic acid.

Literacy

1. Write structural isomers of pent-2-ene.

2. Write cis and trans isomers of following compounds:



3. Write synthesis reaction of but-1-ene from butan-1-ol

Terminology

- stereoisomers -стереоизомерлер /стереоизомеры
- geometric isomers -геометриялық изомерлер / геометрические изомеры
- cracking - крекинг / крекинг

13.3 CHEMICAL PROPERTIES OF ALKENES

Why are saturated fatty acids solid at room temperature while unsaturated fatty acids are liquid?

You will:

- distinguish between electrophilic and nucleophilic particles;
- explain the mechanism of electrophilic addition for alkenes;
- predict the products of addition reactions to asymmetric alkenes
- write the equations of addition reactions: halogenation, hydration and hydrohalogenation;

The chemical properties of alkenes are very different from those of alkanes because of the double bond (C = C) in the structure. Double bond contains a sigma bond and a pi bond. Since electrons in π bonds are bonded less strongly than in sigma bonds. This makes alkenes chemically reactive: combustion, substitution, oxidation and polymerization reactions are all undergone by alkenes.

Oxidation reactions

Combustion reactions

Alkenes burn with oxygen to produce CO2 gas and water. The general equations of combustion is

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

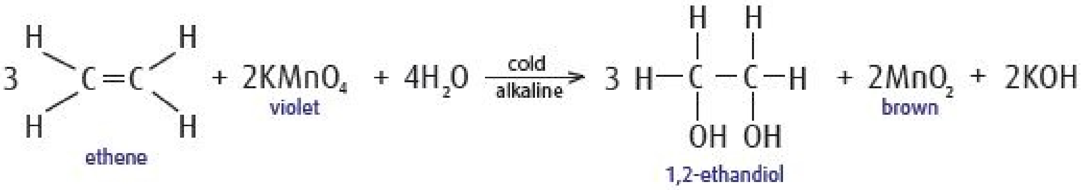
Combustion reactions of ethylene and pentene is

C2H4 + 3O2 → 2CO2 + 2H2O

2C5H10 + 15O2 → 10CO2 + 10H2O

Partial oxidations

Alkenes are easy oxidized. Reactions with dilute potassium permanganate produce vicinal glycols. Decolorization of potassium permanganate solution is used as a test for unsaturation.



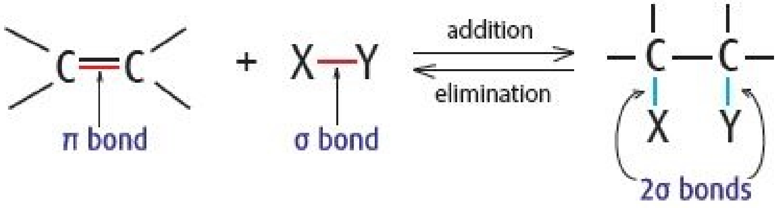
Alkenes oxidized with potassium permanganate in acidic medium to give ketones or carboxylic acids:

$$\underset{\text{2-methylpropene}}{(CH_3)_2C{=}CH_2} \xrightarrow[t^{\circ}]{KMnO_4/H^+} \underset{\text{propane-2-one}}{(CH_3)_2C{=}O} + CO_2 + H_2O$$

$$\underset{\text{but-2-ene}}{CH_3\text{-}CH{=}CH\text{-}CH_3} \xrightarrow{KMnO_4/H^+} \underset{\text{acetic acid}}{2CH_3\text{-}COOH}$$

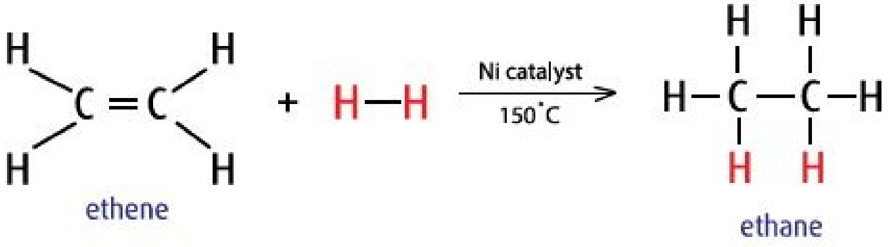
Addition reactions

Addition reactions are characteristic of unsaturated compounds. In addition reactions, an unsaturated bond (C = C) is completely or partially saturated by addition of a molecule across the multiple bond. The most important addition reactions are the addition of hydrogen, the halogens, the hydrogen halides and water.



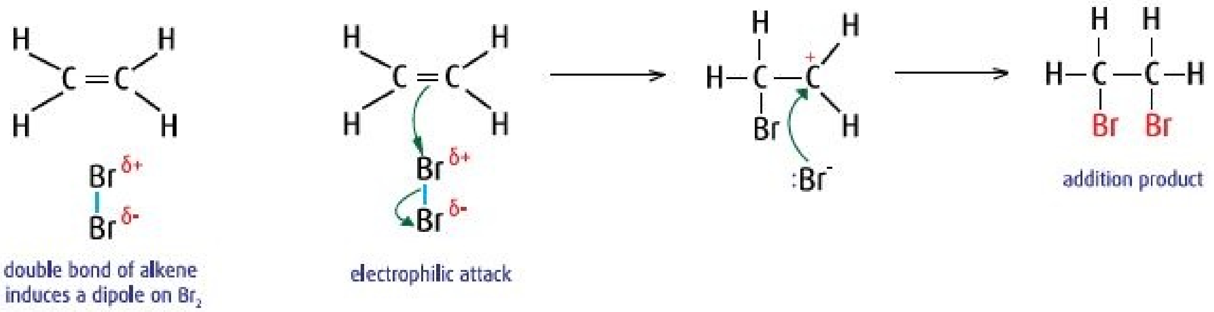
Addition of hydrogen

Alkenes reacted with hydrogen in the presence of Ni/Pd/Pt catalysts:



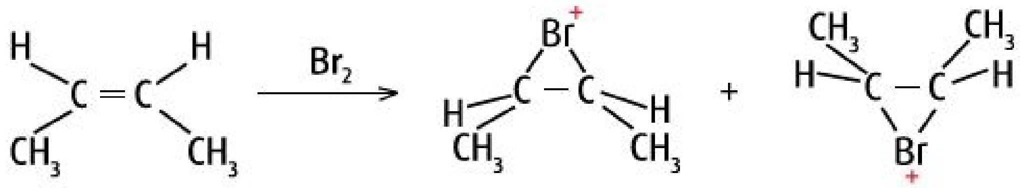
Addition of halogens

Halogens may be added to alkenes at room temperature without a catalyst. One mole of alkene requires one mole of halogen.



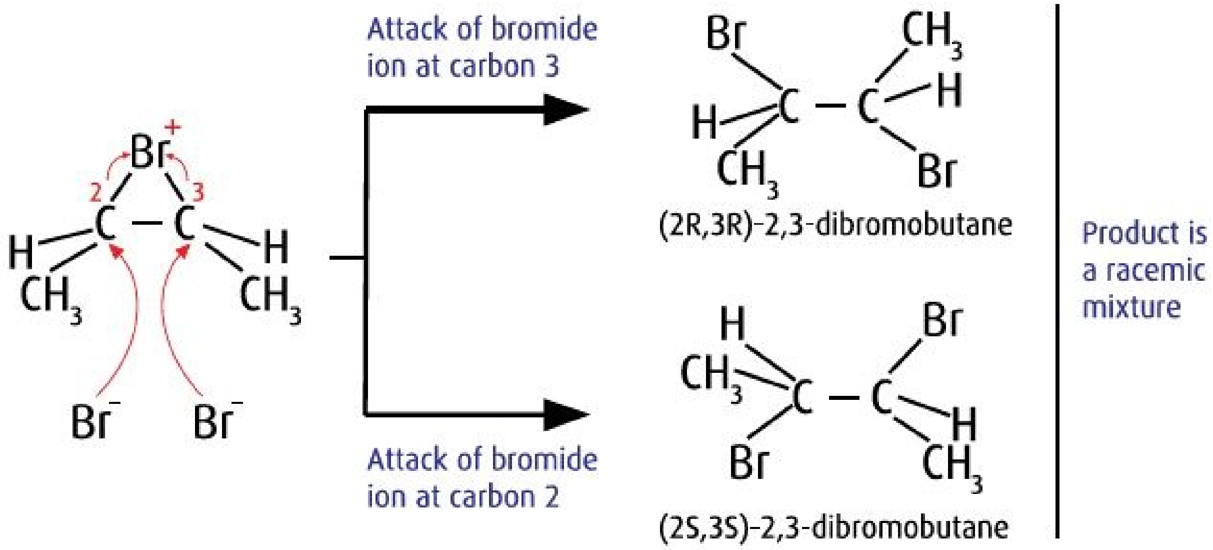
Step 1: Make a new bond between a nucleophile (π bond) and and an electrophile.

Reaction of cis-butene-2 with bromine forms bridged bromonium ions which are meso and identical.



meso bridged bromonium ion intermediate

Step 2: Make a new bond between a nucleophile and an electrophile Attack of bromide at carbons 2 and 3 occurs with equal probability to give enantiomeric products in a racemic mixture.



Addition of hydrogen halides

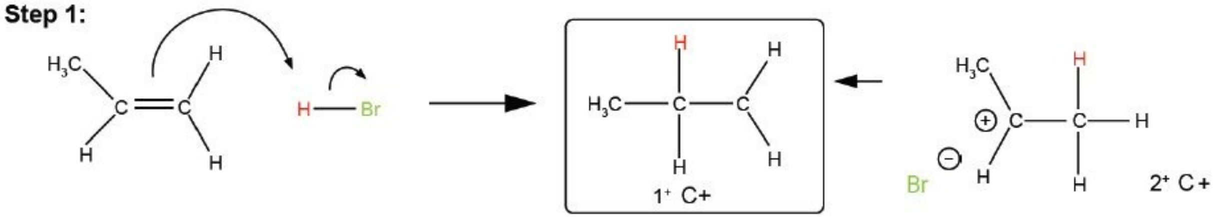
Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism:

$$CH_2=CH_2 + H\text{-}Br \rightarrow CH_3\text{-}CH_2\text{-}Br$$

Markovnikov, a Russian chemist made a generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called Markovnikov rule. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

Mechanism of reaction

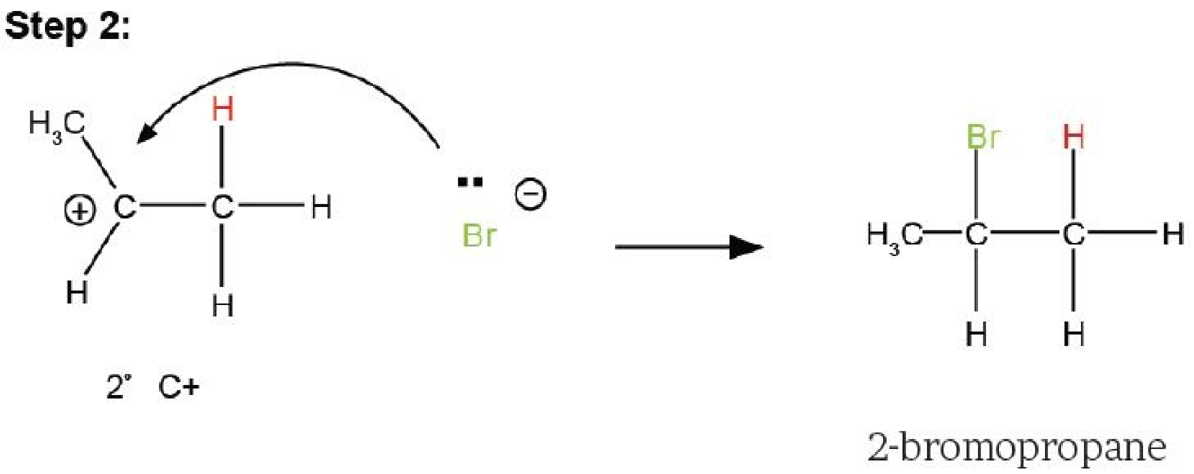
Hydrogen bromide provides an electrophile, H+, which attacks the double bond to form carbocation as shown below:



C+ or carbcations are reactive intermediates that can be stabilized but usually are not isolated.

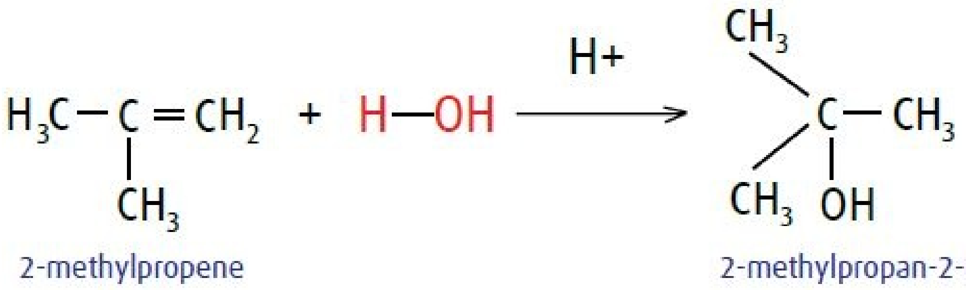
The stability of C+ is 3o > 2o > 1o > methyl.Here only the 2o C+ is formed.

- \- The secondary carbocation (2o C+) is more stable than the primary carbocation (1o C+), therefore, the former predominates because it is formed at a faster rate.
- \- The carbocation (2o C+) is attacked by Br– ion to form the product as follows:



Addition of water

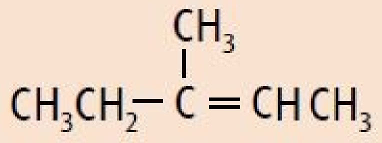
Addition of water (H-OH) to alkenes also occurs according to Markovnikov's rule. Hydrogen (-H) of water is added to the carbon atom of the double bond that already has the greater number of hydrogen atoms. -OH is added to the carbon atom of the double bond that has the smaller number of hydrogen atoms. In this reaction, H2SO4 is used as catalyst, and a monoalcohol is produced.



Literacy

1. Write IUPAC names of the products obtained by addition reactions of HBr to butene-1.

2. Draw structural formulas for the isomeric carbocation intermediates formed on treatment of each alkene with HCl.



$$CH_3CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3$$

$CH_3CH_2CH{=}CHCH_3$

3. Predict the organic product(s) of the reaction of butene-2 with each reagent.

- - H2O (H2SO4)
- - Br2
- - Cl2
- - HI

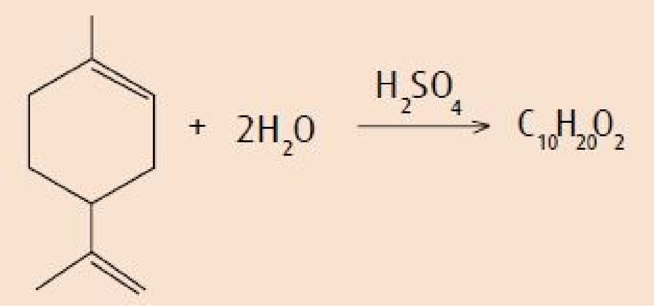
4. Draw a structural formula of an alkene that undergoes acid-catalyzed hydration to give each alcohol as the major product

- - pentanol-2
- - 2-methylbutanol-2
- - propanol-2

5. Reaction of 2-methyl-but-2-ene with each reagent is regioselective. Draw a structural formula for the product of each reaction, and account for the observed regioselectivity.

- - HCl
- - H2O in the presence of H2SO4
- - HBr

6. Terpin, prepared commercially by the acid-catalyzed hydration of limonene, is used medicinally as an expectorant for coughs.



Propose a structural formula for terpin and a mechanism for its formation.

7. Draw the structural formula of the alkenes that reacts with ozone followed by Zn+H2O to give each product or set of products.

- \- $C_4H_8 + O_3(Zn+H_2O)$ → $CH_3CH_2CHO + CH_2O$
- \- $C_4H_8 + O_3(Zn+H_2O)$→ $2CH_3CHO$
- \- $C_3H_6 + O_3(Zn+H_2O)$ →

Terminology

-
- asymmetric -асимметрикалық /асимметричный;
- electrophile - электрофил /электрофил;
- nucleophile - нуклеофил /нуклеофил.

13.4 POLYMERS

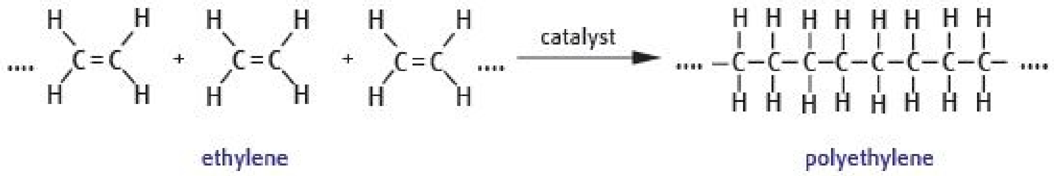
What happens to waste plastic when they are recycled?

You will:

- explain mechanism of polymerization reaction;
- experimentally prove the relative stability of plastics with chemical reagents;
- draw up a scheme for the production of polyethylene;
- name the application areas of polymers.

You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as polymerization.The simple compounds from which polymers are made are called monomers. Other alkenes also undergo polymerization.

The double bonds of the reacting alkenes are converted to single bonds as hundreds or thousands of molecules bond and form long chains. For example, several ethylene molecules react as follows:

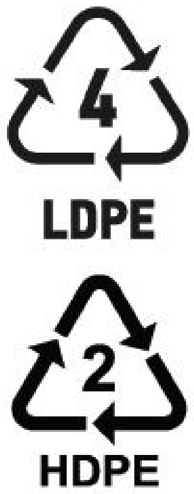


Ethylene polymerizes by a radical mechanism when it is heated at a pressure of 1000-3000 atm at 2500°C with a small amount of an organic peroxide. The properties of polyethylene may change according to the reaction conditions.

$$n\,CH_2{=}CH_2 \xrightarrow[\text{catalysts}]{\text{heat, pressure}} \left(CH_2{-}CH_2\right)_n$$

Polyethylene is the most widely used of all plastics because it is inexpensive, flexible, extremely tough, and chemically resistant. High density polyethylene, HDPE, is used for grocery bags, car fuel tanks, packaging and piping.

Low density polyethylene, LDPE, is softer and more flexible than HDPE. LDPE is used for bottles, garment tags, frozen food packs, film and plastic toys.



Plastic recycling symbols LDPE 4 and HDPE 2

Polyethylene bottle

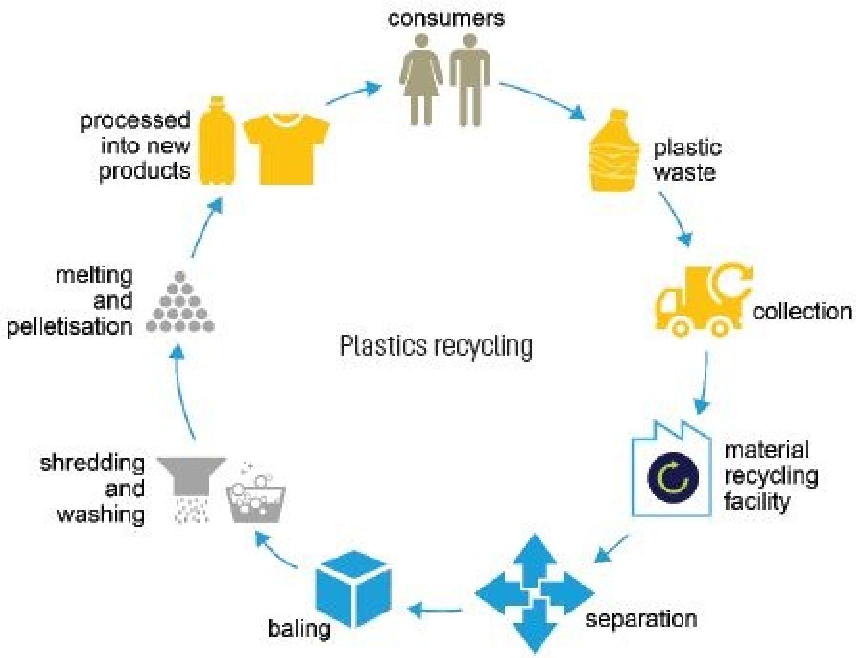
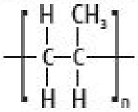
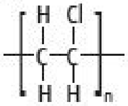
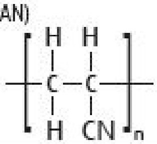
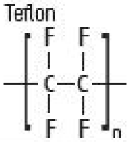
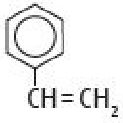
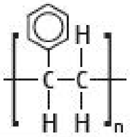
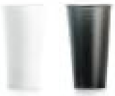
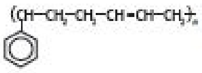
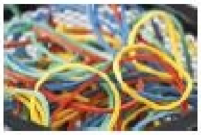

consumers
plastic waste
collection
material recycling facility
separation
baling
shredding and washing
melting and pelletisation
processed into new products
Plastics recycling

Table 22 *Types of polymers*

Monomer	Polymer	Picture	Applications
ethylene $H_2C=CH_2$	polyethylene PE $\left(CH_2-CH_2\right)_n$		plastic piping, bottles, electrical insulation, toys
propylene $CH_2=CH-CH_3$	polyproplylene PP  $\left[-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\right]_n$		film for packaging, carpets, lab wares, toys
vinyl chloride $CH_2=CH-Cl$	polyvinyl chloride (PVC)  $\left[-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-\right]_n$		piping, siding, floor tile, clothing, toys
acrylonitrile $CH_2=CH-CN$	polyacrylonitrile (PAN)  $\left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CN}{C}}-\right]_n$		carpets, fabrics
tetrafluoroethylene $F_2C=CF_2$	Teflon  $\left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\right]_n$		coating for cooking utensils, electrical insulation, earings
styrene 	polystyrene 		containers, thermal insulation, toys
butadiene $CH_2=CH-CH=CH_2$	polybutadiene $\left(CH_2-CH=CH-CH_2\right)_n$		tire tread, coating resin
butadiene and styrene	styrene-butadiene rubber 		synthetic rubber

Chemfact

Polymers opened a new age in the production of rubbers and plastics. Today we use many hundreds of products produced by polymerization reactions. Many sports have been improved with help of polymers and consequently these sports have become more popular than ever. For example, skiers and mountain climbers today have a great advantage over their counterparts of yesteryear. Equipment used for skiing and snowboarding have become much more lighter and ergonomic. The bottom of skies are waxed to decrease friction. In mountain climbing, tools are now made very strong, light and resistant to the natural elements such as wind, sun and the rain.

Literacy

1. Write polymerization reactions of propene and vinylchloride
2. Why are there so many different polymers used by the industry today?
3. What polymers are used in sports equipment?
4. What is the difference between LDPE and HDPE?
5. What is the difference between pipe made from PVC and pipe made from LDPE? Which one is better and why?

Terminology

- polymerization - полимерлену / полимеризация
- grocery bags - зат салатын дорбалар / продуктовые сумки
- garment - киім / одежда
- siding - сырттай қаптау /наружная обшивка
- floor tile - еденге төсегіш /напольная плитка
- skiing - тау шаңғысы /горнолыжный спорт

13.5 ALKADIENES

What do those shoe signs symbols stickers that come with the shoes mean?

You will:

- explain chemical and physical properties of alkadienes;
- study occurrence of dienes in nature and production of rubber.

An alkene is a hydrocarbon which has only one double bond in its structure. Because of the one double bond, they are also called as monoalkenes. Alkenes having two double bonds in their structures are known as "alkadienes". While naming these, instead of the –ene suffix, –diene is used, and carbon atoms having the double bonds are indicated. First member of alkadienes is buta-1,3-diene with unpleasant odor. Isoprene is liquid with boiling point 34°C. General formula of alkadienes is CnH2n-2. Some examples of alkadienes and polyenes are shown as follows.

$CH_2{=}CH{-}CH{=}CH_2$

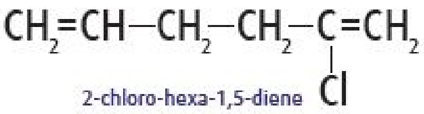
buta-1,3-diene

$CH_3{-}CH{=}CH{-}CH{=}CH_2$

penta-1,3-diene

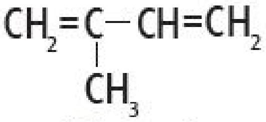
$CH_2{=}C{=}CH_2$

propa-1,2-diene (allene)



$CH_2{=}CH{-}CH_2{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH_2$

2-chloro-hexa-1,5-diene



$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2$

2-methyl-buta-1,3-diene

If an alkene has three double bonds, it is named as shown below, and so on.

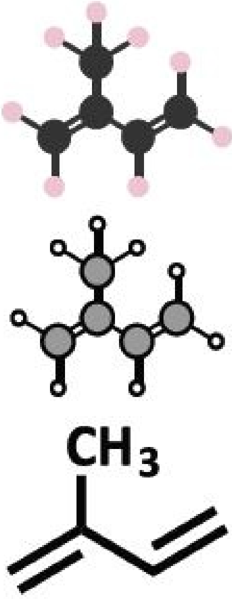
$CH_3{-}CH{=}CH{-}CH{=}CH{-}CH{=}CH{-}CH_3$

octa-2,4,6-triene

Table 23 *Some isomers of pentadiene*

Name	*Molecular formula*	*Structural formula*	*Boiling point (°C)*
pentadiene-1,2	C_5H_8	$CH_2{=}C{=}CH{-}CH_2{-}CH_3$	44.8
pentadiene-1,3	C_5H_8	$CH_2{=}CH{-}CH{=}CH{-}CH_3$	41
pentadiene-1,4	C_5H_8	$CH_2{=}CH{-}CH_2{-}CH{=}CH_2$	26
pentadiene-2,3	C_5H_8	$CH_3{-}CH{=}C{=}CH{-}CH_3$	48.2

The Blue Ridge Mountains are noted for their bluish color due to the Isoprene released into the atmosphere contributing to the characteristic haze and distinctive color.

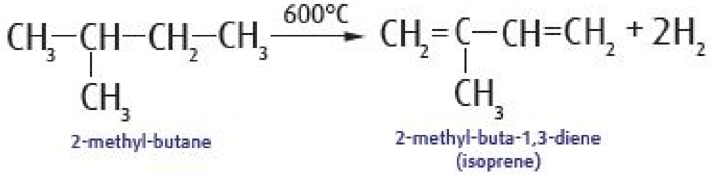


Isoprene structure

Preparation of alkadienes

1. a. From alkanes:

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2 + 2H_2$



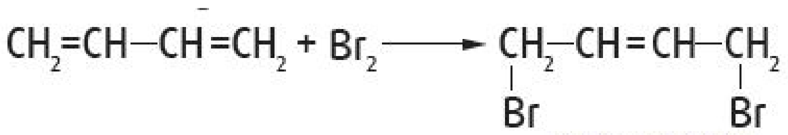
$$\underset{\text{2-methyl-butane}}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2-CH_3} \xrightarrow{600°C} \underset{\text{2-methyl-buta-1,3-diene (isoprene)}}{CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH=CH_2} + 2H_2$$

b. Lebedev's method:

$2CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2\text{=}CH\text{-}CH\text{-}CH_2 + 2H_2 + H_2O$

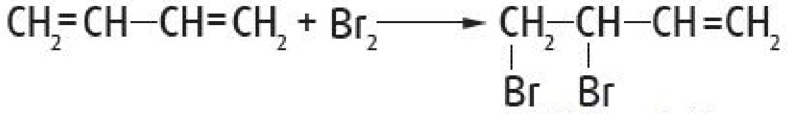
Chemical properties

1. Addition of halogens:



$$CH_2=CH-CH=CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}}-CH=CH-\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

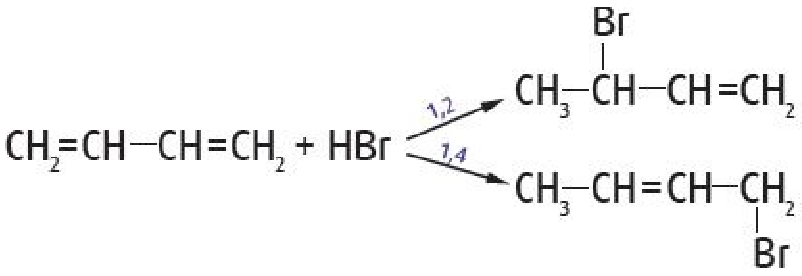
1,4-dibromo-but-2-ene



$$CH_2=CH-CH=CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Br}{\underset{|}{CH}}-CH=CH_2$$

3,4-dibromo-but-1-ene

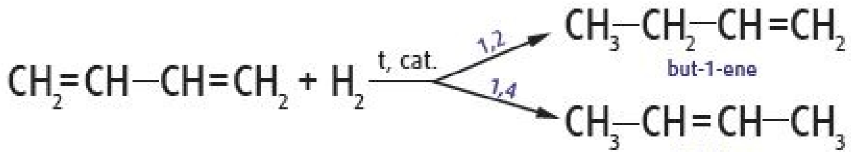
2. Addition of hydrohalogens:



$$CH_2=CH-CH=CH_2 + HBr \xrightarrow{1,2} CH_3-\overset{\displaystyle Br}{\overset{|}{CH}}-CH=CH_2$$

$$CH_2=CH-CH=CH_2 + HBr \xrightarrow{1,4} CH_3-CH=CH-\underset{\displaystyle Br}{\underset{|}{CH_2}}$$

3. Addition of hydrogen:



$$CH_2=CH-CH=CH_2 + H_2 \xrightarrow[1,2]{t,\ cat.} CH_3-CH_2-CH=CH_2$$

but-1-ene

$$CH_2=CH-CH=CH_2 + H_2 \xrightarrow[1,4]{t,\ cat.} CH_3-CH=CH-CH_3$$

but-2-ene

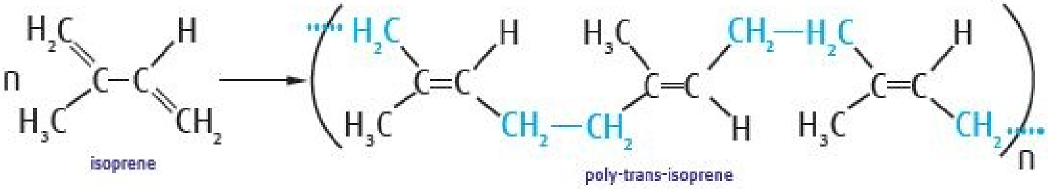
Polymers of butadiene derivatives

The derivatives of butadiene are natural rubber and synthetic rubber.

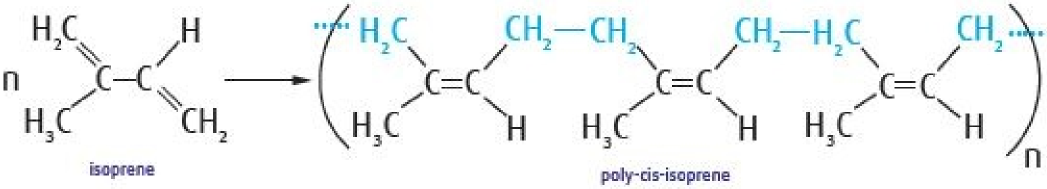
Natural Rubber

Natural rubber is extracted from the hevea brasiliensis tree which is grown in tropical regions. When its bark is slit with a cutter, a liquid, named latex, is obtained. Latex is an emulsion of rubber in water. When acid is added to this emulsion, natural rubber is precipitated. This precipitate is the polymer of a hydrocarbon with the molecular formula C5H8.

The common name of this compound is isoprene and its IUPAC name is 2–methylbutadiene-1,3. Polymerization of isoprene gives polyisoprene, natural rubber. Polymerization may lead to cis or trans versions of polyisoprene.



The trans–isomer is stiffer than the cis-polymer and used in the production of golf balls, golf clubs, and tennis-rackets.

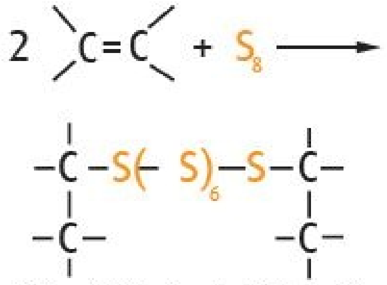


Milky latex extracted from rubber tree

Rubber sheet

Natural rubber with its natural structure is a sticky substance with low elasticity which isn't very useful to the chemical industry. However, when natural rubber is heated with sulfur, it becames harder, less soluble and more durable and so much more useful. This process is known as vulcanization.

If the percentage of sulfur is 1-5%, a soft rubber is produced. Soft rubber is used in the production of shoe soles, car inner tubes, plastic gloves and many more different products. The rubber used in car tyres is produced if the proportion of sulphur is 30-50%.



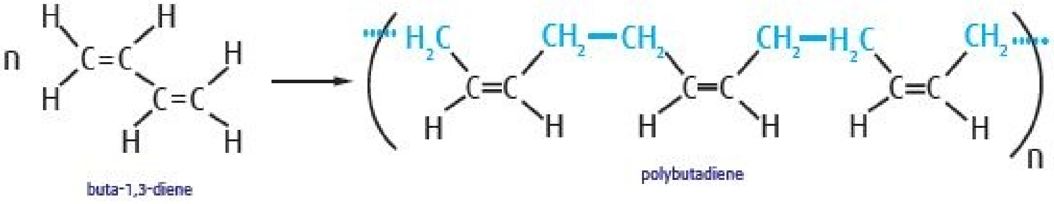
S_8 is added to the double bond of the alkene in the vulcanization process

Car tires

A vulcanized product of rubber

Synthetic rubber

After the usage of natural rubber became widespread, scientists started to investigate the production of synthetic rubber. In 1920, a German chemist produced an artificial rubber by polymerizing butadiene obtained from petroleum. This rubber was named BuNa rubber (Bu from butadiene and Na from the sodium which was used as the catalyst in the reaction).



Synthetic rubber is flexible

After the production of polybutadiene, the automotive industry developed very rapidly. Car tyres, interior and exterior parts of cars could now be produced from artificial rubber.

Chemfact

In 2010, Nike carries out the following action: material obtained from the recycling of 13 million plastic bottles was used for the production of T-shirts (an average of 8-9 bottles for one T-shirt), including representatives of 10 national football teams EURO-2012.

Chemfact

In 1839, Charles Goodyear (1800-1860) vulcanized rubber by heating natural rubber with sulfur. Instead of a lowelastic, sticky product being formed, a more elastic and stronger polymer was formed. According to the percentage of added sulfur, the properties of the rubber vary.

Literacy

1. Draw the structural formula for the following compounds. Name all the
compounds.

- \- C_6H_{10}
- \- C_5H_8

2. Find the molecular formula of the alkadiene that contains 11.11% hydrogen by mass.

3. Write the equations for the reactions between butadiene-1.3 and the given
substances. Name the products.

- \- H_2
- \- Br_2

- - HBr

4. Write out the preparation reactions of butadiene-1,3.

5. How many σ bonds are there in an alkadiene whose molecular weight is 54 grams?

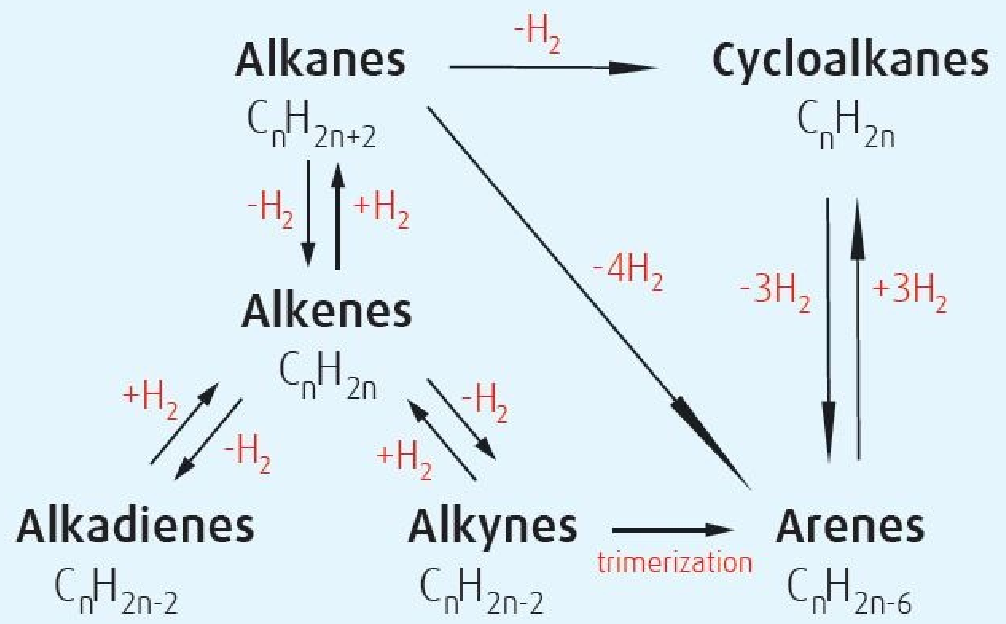
6. What is the molecular formula of 2,3,4-trimethylpentadiene-1,3?

7. 20 liters of air is needed to burn 5 liter of an alkadiene. What is the molecular formula of this alkadiene?

Terminology

- alkadienes - алкадиендер /алкадиены
- rubber - каучук
- vulcanization - вулканизация

THE RELATIONSHIP BETWEEN HYDROCARBONS



13.6 ALKYNES

Why does acetylene burn with a sooty flame?

You will:

- make structural formulas of alkynes, study chemical properties and preparation methods of alkynes.

Hydrocarbons that contain the carbon-carbon triple bond -C≡C- are called alkynes. Each triple bond contains one sigma (σ) and two pi (π) bonds. Because of the π bonds in their structure alkynes are unsaturated hydrocarbons.

The general formula of alkynes is CnH2n–2 where n is an integer starting from 2.

The first member of the alkynes is acetylene (ethyne). The common name for alkynes is the acetylenes.

Alkynes are named by using the -yne suffix in place of the -ane suffix of alkanes.

$HC \equiv CH$

C_2H_2

acethylene

$HC \equiv CCH_3$

C_3H_4

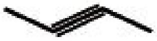
propyne

$HC \equiv CCH_2CH_3$

C_4H_6

butyne-1

$CH_2C \equiv CCH_3$



C_4H_6

butyne-2

The physical properties of alkynes are similar to those of alkanes and alkenes.

They are insoluble in water but quite soluble in organic solvents.

Densities of liquid alkynes are less than that of water.

At room temperature, the first three members of the series (ethyne, propyne and butyne) are gases, the others are liquids.

Acethylene ballons

Acethylene is highly flammable gas

Chemical properties

Alkynes undergo combustion reactions and addition reactions, as alkenes do. In addition, alkynes undergo substitution reactions with metals.

1. Combustion reactions

Alkynes produce CO2 and H2O when they are burnt with a sufficient amount of oxygen:

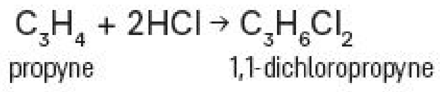
$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$
$$C_3H_4 + 4O_2 \rightarrow 3CO_2 + 2H_2O$$

2. Addition reactions

Addition reactions occur by breaking the π bonds of the triple bond. Hydrogen, halogens, hydrogen halides and water may give addition reactions with alkynes.

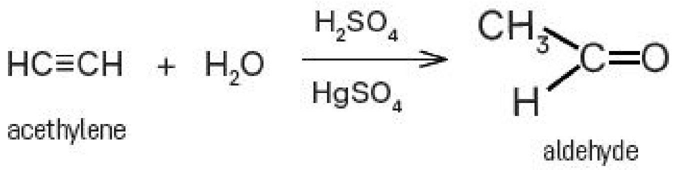
$$C_2H_2 + H_2 \xrightarrow{cat.} C_2H_4$$
$$C_2H_4 + H_2 \xrightarrow{cat.} C_2H_6$$

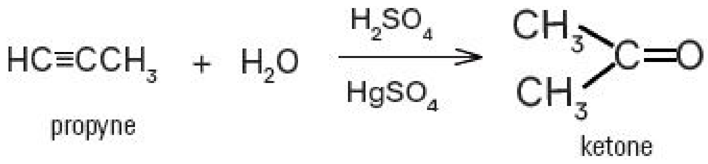
Hydrogen halides, HX, are added to alkynes according to Markovnikov's rule.



$C_3H_4 + 2HCl \rightarrow C_3H_6Cl_2$

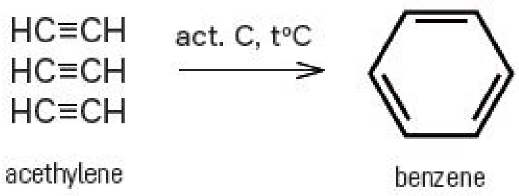
A mixture of mercury (II) sulfate, HgSO4, and sulfuric acid enables water to add to alkynes. When water is added to acetylene (HC=CH) acetaldehyde forms.





3. Trimerization

When acetylene is passed through a red hot copper tube, benzene is formed.



Preparation

1. The preparation of acetylene from calcium carbide is the most important preparation method. When quicklime and coke react with each other at high temperature, calcium carbide is formed. The reaction of calcium carbide with water produces acetylene.

$$CaO + 3C \xrightarrow{2000^\circ C} CaC_2 + CO$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

2. Dehalogenation of dihaloalkanes.

$$CH_3\text{-}CHBr\text{-}CH_2Br + 2KOH \xrightarrow[\text{alcohol}]{t^\circ C} CH_3\text{-}C{\equiv}CH + 2H_2O + 2KBr$$

Literacy

1. What is the difference between alkane, alkenes and alkynes?
2. Which is more stable, alkane, alkene, or alkyne?
3. What is the molecular formula of an alkyne of which 0.63 grams contains 0.07 grams of H?
4. When 5 grams of impure CaC2 is added to water, 1.12 L of acetylene is produced at STP. What is the percentage purity of the CaC2 sample?
5. Starting from CaCO3, obtain
a. acetylene
b. ethylene
c. ethane
6. 2.24 L H2 at STP is needed to saturate 2 grams of an alkyne? What is the molecular formula of this alkyne?

Chemistry around us

Oxygen-acetylene flame is used for iron welding.

Chemistry around us

In industry acetylene used for synthesis of acetaldehyde, acetic acid, ethanol, plastics and polymers.

13.7 PETROLEUM. COMPOSITION OF PETROLEUM. PETROLEUM PRODUCTS

How oil (petroleum) harms animals and plants in marine environments?

You will:

- explain the processes of oil fractionation and the use of fractions;
- explain processes of catalytic and thermal cracking;
- know the composition and production of the most important products from natural and associated gases, coal.

Kazakhstan has the largest oil (petroleum) and gas reserves in the Caspian Sea basin, and it is producing 1.5 million barrels of oil a day today. Kazakhstan contains significant quantities of gas and oil in particular. Kazakhstan sits near the northeast portion of the Caspian Sea and claims most of the Sea's biggest known oil fields. Oil has been produced in Atyrau, Mangystau, Aktobe and Kyzylorda regions. Crude oil is a mixture of alkanes and aromatic hydrocarbons which have carbon atom numbers ranging from 1 to 40. In different regions of the world the composition of oil is different.

Petroleum, or crude oil, is a naturally occurring bituminous liquid composed of many different organic compounds. Liquid petroleum, depending upon the percentages of compounds, is a green-dark brown color of variable darkness.

Formation of Petroleum

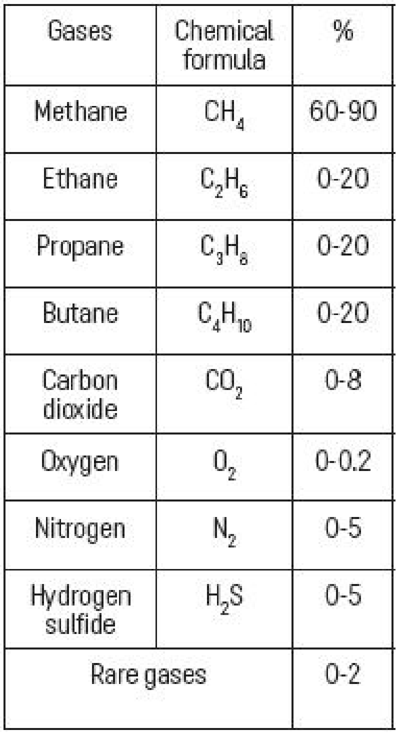
Petroleum is formed underneath the Earth's surface by the decomposition of marine organisms and fossils of prehistoric animals and plants. The remains of tiny organisms that live in the sea, or land organisms that are carried down to the sea in rivers, are trapped by sands at the sea bottom. These deposits become the main source of crude oil. As additional deposits build up, the pressure on the ones below increase a thousand fold and temperature reaches a hundred degrees. The remains of the dead organisms are transformed into crude oil and natural gas.

Refining

Crude oil in its natural form can only be used as a fuel, and not in any other areas. Because it consists of many different substances with different densities, petroleum can be separated into its components by fractional distillation. Before fractional distillation, petroleum is refined by a pre-distillation method so that undesired components are driven out of the petroleum mixture. After that, the petroleum is pumped through heated pipes at 350-4000C. Here, the petroleum becomes vapor and this is sent to the fractional distillation unit. The petroleum vapor starts rising to the upper parts of the fractional distillation unit. The vapor of petroleum cools down at lower temperatures; the uppermost part of the distillation unit is the place for gases (methane, ethane, propane and butane), which have boiling points lower than 200C; C3H8 and C4H10 are separated from each other at high pressures and stored in canisters for home use.

Gasoline is produced by catalytic cracking and reforming. Gasoline is used as a fuel in engines designed to run on unleaded gasolines. Jet fuel is a type of aviation fuel designed for use in aircraft powered by gas turbine engines. Diesel oil is a heavy oil that is used to power diesel engines. The most commonly used form of diesel is derived from petroleum, but other forms of diesel oil also exist. Synthetic diesel oil is used to fuel cars, trucks, and some aircraft . Motor oil (engine oil, lubricating oil) is an oil used for lubrication of various internal combustion engines. The main function is to lubricate moving parts. Fuel oil is a lighter type of oil, or a liquid byproduct of crude oil, which is used for energy, especially in regard to heating. Cracking is the process whereby complex organic molecules such as heavy hydrocarbons are broken down into simpler molecules such as light hydrocarbons.

Pouring crude oil

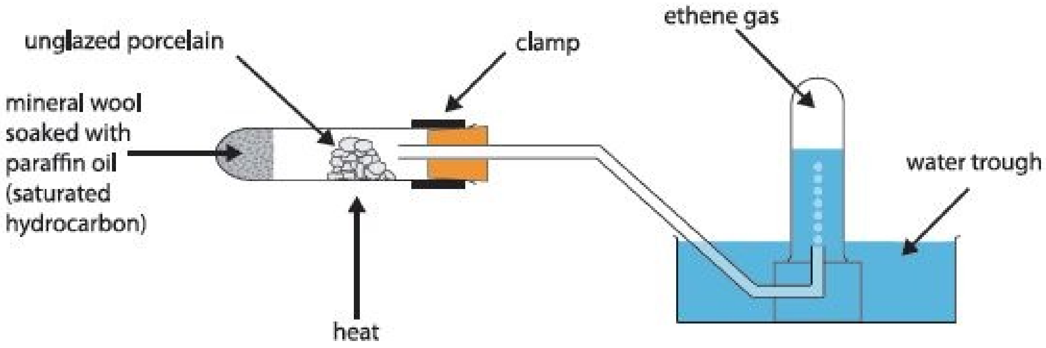


Gases	Chemical formula	%
Methane	CH_4	60-90
Ethane	C_2H_6	0-20
Propane	C_3H_8	0-20
Butane	C_4H_{10}	0-20
Carbon dioxide	CO_2	0-8
Oxygen	O_2	0-0.2
Nitrogen	N_2	0-5
Hydrogen sulfide	H_2S	0-5
Rare gases		0-2

Chemical composition of natural gas

C	64.46%
H	2.32%
N	1.20%
O	6.20%
S	1.04%
Moisture	2.05%
Ashes	26.00%

Elemental composition of natural gas



Laboratory cracking of paraffin oil

In the cracking process higher alkanes are converted into smaller alkanes and alkenes at high temperatures. When a catalyst is used in the process, it is known as catalytic cracking.

$$CH_3(CH_2)_8\dot{C}H_3 \rightarrow CH_3(\bar{C}H_2)_6CH_3 + C_2H_4$$

Petroleum refineries convert crude oil and other liquids into many petroleum products that people use every day

Literacy

1. Answer the following questions about diesel, paraffin, naphtha, gasoline.
a. Which product has the highest boiling point?
b. Which product has the lowest boiling point?
c. Which product has the highest melting point?
2. What is petroleum, and where does it come from?
3. What are petroleum products, and what is petroleum used for?
4. How to distillate crude oil in the laboratory?
5. How will electric cars affect the oil industry?
6. Why is cracking used in the oil industry?

Chemistry around us

Crude oil that leaks into the sea forms an insoluble layer on the surface.

Chemfact

Oil was formed from organic material (the remains of living organisms), but these were organisms significantly smaller than dinosaurs. According to scientists, the source material for the formation of oil was microorganisms inhabiting the coastal seawater - plankton, 90% of which is phytoplankton.

Terminology

- cracking - крекинг
- refining - өңдеу /переработка.

QUESTIONS AND PROBLEMS

1. Write IUPAC names of the following compounds:

- - CH3CH=C(CH3)2
- - CH3CH2CH2CH2CH=CH2
- - CH3CH=CHCH2CH2CH2

2. Draw structural formulas for these alkenes:

- - cis-2-methyl-hexene-3
- - 2-methyl-butene-1
- - 2,3-dimethyl-butene-1
- - (Z)-1-chloropropene
- - 3-methyl-hexene-3
- - trans-pentene-2
- - tetrabromoethylene

3. Calculate the index of hydrogen deficiency for pentene-2, C5H10, and account for this deficiency by reference to its structural formula.

4. Calculate the index of hydrogen deficiency for pentene-2, C5H10, and account for this deficiency by reference to its structural formula.

5. For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double bond as indicated:

- - C4H8 (one double bond)
- - C5H10 (one double bond)

6. Write chemical equations for combustion reaction of the following alkenes:

butene-1; hexene; ethylene; propene

7. Draw the cis and trans structures of pentene-2.

8. Write structures and IUPAC names of different structural isomers of alkenes corresponding to C6H12.

9. Write structural isomers of butene-2.

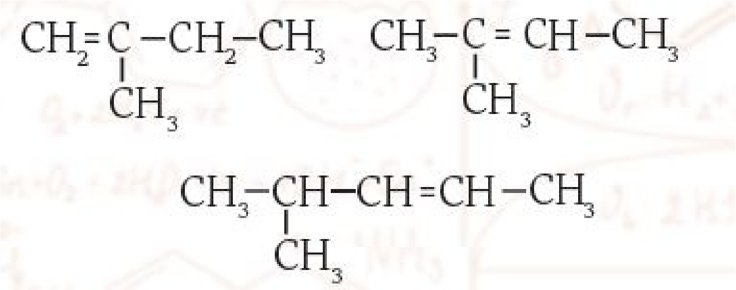
10. Draw cis- and trans- isomers of the following compounds. Also write their IUPAC names:

- - CHBr = CHBr
- - C2H5CH = CHC2H5

11. Which of the following compounds will show cis-trans isomerism?

- - CH3CH = CClCH3
- - C2H5CH = CCl2
- - C2H5CH = CHCH3

12. Determine which of the following can exhibit geometric isomerism, and draw structural formulas for the cis and trans isomers of those that can:



$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2{-}CH_3 \qquad CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH{-}CH_3$

$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH{-}CH_3$

13. Write synthesis reactions of propene from propanol-1 and propyne.

14. Complete the following reactions:

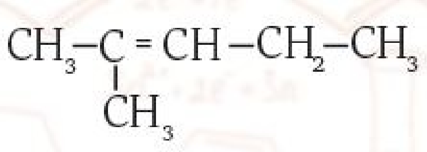
- - HC=CH + H2 →

- - CH3-CH2-CCH + 2H2 →
- - CH3-CH(Cl)-CH3 + KOH(alcohol) →
- - CH3-CH2-CH2-Cl + KOH(alcohol) →
- - CH3-CH2-CH2-Br + Zn →
- - CH3-CH(OH)-CH3 dehydration

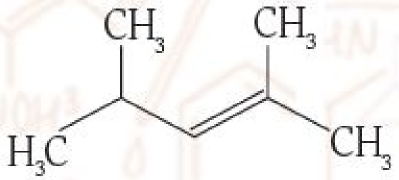
15. Show how to convert propene to these compounds:

- - propane
- - propanol-1
- - 1-bromopropane
- - 1-iodopropane

16. Write IUPAC names of the products obtained by addition reactions of HCl to pentene-1.



$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_2-CH_3$



17. Draw structural formulas for the isomeric carbocation intermediates formed on treatment of each alkene with HCl.

18. Predict the organic product(s) of the reaction of pentene-2 with each reagent.

- - H2O (H2SO4)
- - Br2
- - Cl2

19. Draw a structural formula of an alkene that undergoes acid-catalyzed hydration to give each alcohol as the major product:

- - pentanol-2
- - 2-methyl-propanol

20. Reaction of 2-methyl-butene-2 with each reagent is

regioselective. Draw a structural formula for the product of each reaction, and account for the observed regioselectivity.

- \- HBr
- \- H_2

21. Draw the structural formula of the alkenes that reacts with ozone followed by Zn+H2O to give each product or set of products.

- \- $C_5H_{10} + O_3(Zn+H_2O) \rightarrow CH_3\text{-}C(O)\text{-}CH_3 + CH_3CHO$
- \- $C_4H_8 + O_3(Zn+H_2O) \rightarrow 2CH_3CHO$

22. Write polymerization reactions of ethylene and propylene

23. What polymers are used in medicine and chemistry laboratory?

24. Write polymerization reaction of isoprene

25. Write preparation reaction of penta-2,4- diene from pentane.

26. Write structural formulas of all isomers of C_5H_8.

27. Why is rubber used to make tires? What are the raw materials for rubber production?

14
CHAPTER

HALOALKANES

CHAPTER 14: HALOALKANES

14.1 HALOALKANES. PREPARATION OF HALOALKANES

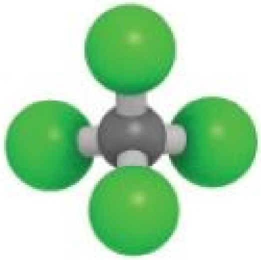
Why are haloalkanes more reactive than alkanes?

You will:

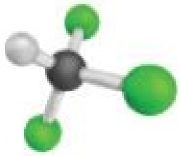
- know what haloalkanes are;
- know the preparation of haloalkanes.

Haloalkanes

Haloalkanes (alkyl halides) are saturated aliphatic organic compounds that contain "carbon-halogen" bonds in their composition. Haloalkanes are very important for the synthesis of many compounds. Replacement of hydrogen atoms with halogen makes the compound chemically active since the bond of carbon with the more electronegative halogen atom is polar making it quite reactive in ion type reactions. The polarity of a covalent bond, for example, C-Cl, leads to a shift in the electron density of the bond towards chlorine.



Carbon tetrachloride molecule



Chloroform molecule

Physical properties of haloalkanes

Most haloalkanes in pure form are colorless compounds. Physical properties depend not only on the alkyl group to which the halogens are bound but also on the halogen itself, and the number of atoms in the molecule. Haloalkanes are insoluble in water but soluble in organic solvents. Halogen-methanes are gases (except iodomethane) and have a sharp odor.

For haloalkanes, the following trends in the variation of physical properties can be determined:

1. The boiling points and density of haloalkanes show an increasing trend in transition from primary to secondary and tertiary halogenalkanes.

2. As the number of halogen atoms increases, the melting and boiling temperatures of the haloalkanes increase, this is because the molecular weight of the compounds increases sharply (halogen atoms are "heavy" atoms), except polyfluorinated alkanes.

3. A feature of the physical properties of haloalkanes is a reduction in the melting and boiling point of a compound containing 2 or 3 halogen atoms per carbon atom, as compared to an isomer having halogen atoms for different carbon atoms.

4. In general, iso-structured haloalkanes have lower melting and boiling points than their isomers of normal structure.

Table 24 *Physical properties of haloalkanes*

Compound	Boiling point (°C)
Methyl chloride CH_3Cl	-24
Dichloromethane CH_2Cl_2	40
Trichloromethane (chloroform) $CHCl_3$	61
Tetrachloromethane CCl_4	77

Table 25 *Physical properties of haloalkanes*

Compound	Structural formula	Melting point (°C)	Boiling point (°C)
Fluoromethane	CH_3-F	-141,8	-78,5
Chloromethane	CH_3-Cl	-97,7	-23,7
Bromomethane	CH_3-Br	-93,7	3,6
Iodomethane	CH_3-I	-66,5	42,5

Preparation of haloalkanes

Haloalkanes can prepared by substitution reactions and addition reactions.

1. Halogenation of alkanes

Halogenation of alkanes is a substitution reaction of one or more hydrogen atoms in an alkane molecule by halogen. The reaction products are called haloalkanes or halogenated alkanes. The reaction of alkanes with chlorine and bromine goes on light or with heating.

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

(hv - quantum of light)

With a sufficient amount of chlorine, the reaction proceeds further and leads to the formation of a mixture of substitution products of 2, 3, and 4 hydrogen atoms:

$CH_3Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + HCl$ dichloromethane
$C_2H_2Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$ trichloromethane
$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$ tetrachloromethane

The reaction of halogenation of alkanes proceeds via a radical chain mechanism, i.e. as a chain of successive transformations involving freeradical particles.

The mechanism of radical substitution (symbol SR)

Step 1: Nucleation of the chain - the appearance of free radicals in the reaction zone. Under the action of light energy, the bond in the molecule Cl:Cl is homolytically destroyed by two chlorine atoms with unpaired electrons (free electrons) •Cl:

$Cl_2 \xrightarrow{h\nu} 2Cl\bullet$

Step 2: Growth (development) of the chain. Free radicals, interacting with molecules, generate new radicals and develop a chain of transformations:

$Cl\bullet + CH_4 \rightarrow HCl + \bullet CH_3$
$\bullet CH_3 + Cl_2 \rightarrow CH_3Cl + \bullet Cl$

Step 3: Chain termination. Radicals, connecting with each other, form molecules and terminate the chain of transformations:

$\bullet CH_3 + Cl\bullet \rightarrow CH_3Cl$
$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$

In the chlorination or bromination of an alkane with secondary or tertiary carbon atoms, hydrogen is most easily replaced by a tertiary atom, more difficult for a secondary one, and even more difficult for a primary one. This is explained by the greater stability of tertiary and secondary hydrocarbon radicals compared with the primary ones due to delocalization of the unpaired electron. Therefore, for example, in bromination of propane, the main reaction product is 2-bromopropane:

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{hv} CH_3CH(Br)CH_3 + HBr$$

2. Hydrochlorination of unsaturated hydrocarbons:

$$CH_2{=}CH_2 + HCl \rightarrow CH_3Cl$$

3. Obtaining from alcohols:

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

Literacy

1. Draw the structures of all isomers that have the molecular formula C2H5Cl.

2. Show all the possible structural formulas of C3H5Cl3.

3. Write the structures of the following organic halogen compounds:

iodoform, 2-bromobutane, 3-chloropentane, 1-chloro-2,2-dimethylpropane

4. 7. Derive the empirical formula of a haloalkane that on analysis gave the following percentage composition: C=10%, H=0.88%, Cl=89.12%.

5. A scientist uses the chlorine Cl2, in the synthesis of CCl4 according to the given reaction equation: 3Cl2 + CH4 → CHCl3 + 3HCl

What mass of Cl2 gas should be used to synthesize 45 g CHCl3? Assume that the yield of the reaction is 80%.

Chemfact

Poisonous plume of smoke at Hawaii's Kilauea Volcano. Chloromethane (CH3Cl) is also found in emissions from volcanoes such as Hawaii's Kilauea.

Chemistry around us

Dichloromethane, trichloromethane and tetrachloromethane are used as organic solvents

Terminology

- haloalkanes -галогеналкандар /галогеналканы
- substitution - орынбасу /замещение
- free-radicals - бос радикалдар / свободные радикалы
- nucleation - бөліну /образование
- termination - тоқтау /прекращение

14.2 ENVIRONMENTAL EFFECTS OF HALOALKANES

Pesticides are used to increase number of produced crop, however it can negatively affect the environment. What is the solution for this problem?

You will:

- know the usage of some important haloalkanes
- identify the environmental problems associated with the influence of halogenoalkanes;

Usage and environmental effects of haloalkanes

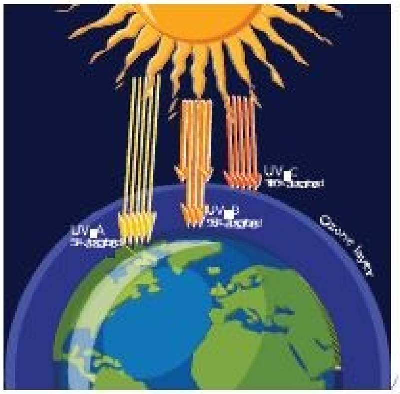
Halogenalkanes (haloalkanes) as its name implies, are alkanes with at least one hydrogen atom replaced to halogen. Haloalkanes are important intermediates in the synthesis of a wide variety of substances. Some uses of haloalkanes are given below.

Freons are the technical name of polyhaloalkanes, which were used as refrigerants. Most often they were used in air conditioners and refrigerators. It is assumed that freons contribute to the destruction of the protective ozone layer in the upper atmosphere. This ozone layer protects the Earth's atmosphere from the dangerous effects of ultraviolet radiation from the sun, because the destruction of the ozone layer can cause serious damage to all living organisms. Freons were used not only in refrigeration machines, where they can accidentally get into the atmosphere but also in aerosol cans, although such use is now condemned.

1,2-Dibromoethane (ethylene dibromide) has long been used as a fumigant, until in 1984 its carcinogenic effect was found. Now its use in some countries is prohibited.

1,2-Dichloroethane (ethylene dichloride) is used as a solvent to remove stains from clothing and fabrics.

Carbon tetrachloride $CCl4$ and chloroform (trichloromethane) $CHCl3$ are used in the laboratory as solvents. However, certain precautions must be taken, since these substances are hazardous to health. Carbon tetrachloride was used for dry cleaning clothes and sometimes to extinguish fires. But, since the exposure of carbon tetrachloride to the flame produces poisonous substances, its use is limited. Chloroform was used as an anaesthetic.



Ozon layer

Removing gases from the freon tubes

Molecular model of liquid CCl_4

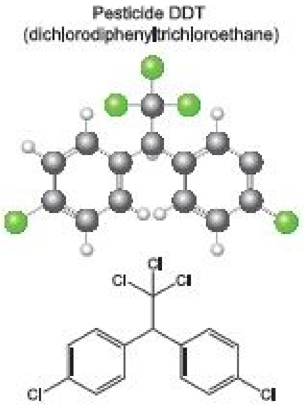
Dichlorodiphenyltrichloroethane (DDT) and analogues

Insects can destroy a significant part of the crop. Therefore, the cultivation of some crops on large areas is almost impossible without the use of insecticides. One of the most effective substances is the powder DDT - Dichlorodiphenyltrichloroethane.

Chemically pure DDT is an odorless crystalline powder. It is soluble in organic solvents. In water, it only forms an emulsion. According to the results of numerous studies, chemists came to the conclusion that a chemically pure drug DDT is toxic for fish, insects, cold-blooded and some warm-blooded representatives of the animal world. The drug is toxic to large warm-blooded creatures and human, but without fatal outcome.

Chemically pure insecticide DDT was highly effective in combating the carriers of epidemic diseases (mosquitoes, fleas, mosquitoes), pests of crops, including locusts. Its high toxicity is confirmed by the following example: for the death of the larva of the housefly, it is sufficient to contact one-millionth milligram of powder. The drug was economically advantageous: once treated surface remains deadly for insects for a long time and does not require re-treatment.

Fogging DDT spray to kill mosquito for control Malaria



DDT molecule

Danger of exposure to DDT on human health

When insecticides are used to kill insects, it enters the food chain. Repeated use of contaminated crop in human food, no doubt, contributes to the accumulation of DDT in the body. Residual quantities of it accumulate over time, although extremely slowly, but constantly. From the human body, DDT can be excreted by the mother's milk and passed on to the newborn. Therefore, it can be found in the second and subsequent generations, whose ancestors have received certain amounts of DDT with food or other means. When you consume large amounts of food containing high amounts of DDT, the negative health effects are felt causing illness and discomfort, but they do not cause immediate death. Also it may have negative impact on animals and fish because its accumulation reduces the reproductive function of birds and some mammals, including bats. It is highly toxic to cold-blooded invertebrates and fish.

Literacy

1. What is the molar mass of chloroform?

2. What type of haloalkane is made when the halogen atom is bonded to a carbon atom?

3. How to synthesis chloroform in industry?

4. Does Freon gas harmful to the human body?

5. What would a chemical equation of freon and ozone look like?

6. How does DDT affect water ecosystems?

Chemistry around us

Bromochlorodifluoromethane and bromotrifluoromethane are used in fire extinguishers.

Activity

Pesticides are important compounds in a agriculture. Write a short text describing about pesticide effects. Write a short text describing this process. Use the internet and chemistry books to help you. Include the following information:

- - benefits of pesticides
- - health effects
- - types of pesticides

Terminology

- influence - әсер / влияние
- intermediate - аралық /промежуточный
- refrigerant - суытқыш /хладагент
- cultivation - қопсыту /культивирование
- insecticide - инсектицид /инсектицид

14.3 REACTIONS OF NUCLEOPHILIC SUBSTITUTION OF HALOALKANES

How to produce unsaturated hydrocarbons from haloakanes?

You will:

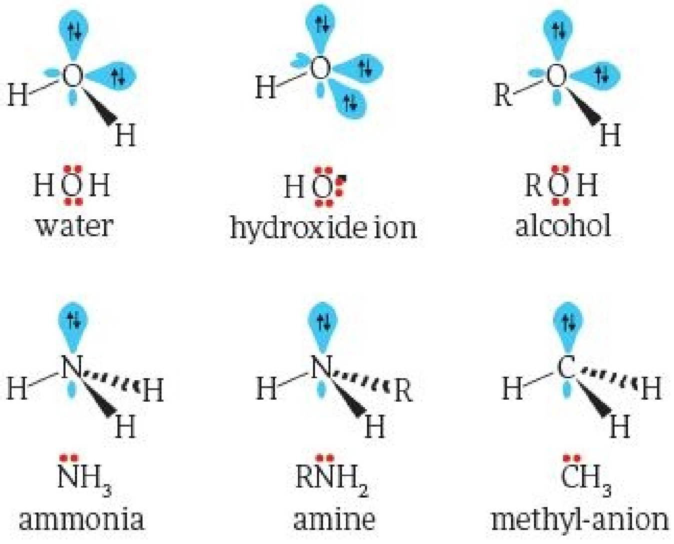
- know what nucleophilic reactions;
- write equations for the reactions of haloalkanes with nucleophilic reagents;
- explain the reaction mechanisms of nucleophilic substitution of haloalkanes.

Nucleophilic reactions

Nucleophilic reaction is a reaction in which a molecule of an organic substance is exposed to the action of a nucleophilic reagent. Nucleophilic ("nucleus-loving") reagents, or nucleophiles are particles (anions or molecules) that have an unshared pair of electrons in their valence shell.

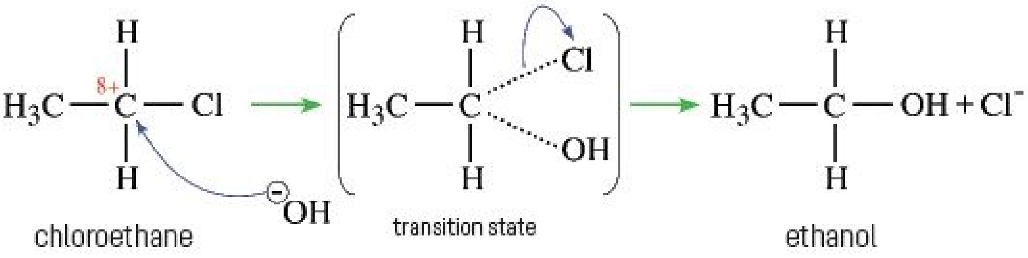
Examples of nucleophilic particles: OH-, Cl-, Br-, CN-, H2O, CH3OH, NH3.

Structures of some nucleophilic reagents:



Structures of some nucleophilic reagents

Due to the mobility of p-electrons, nucleophilic properties are also possessed by molecules containing p-bonds: CH2=CH2, CH2=CH-CH=CH2, C6H6, etc. Example of nucleophilic reaction:



, where OH- is a nucleophilic reagent.

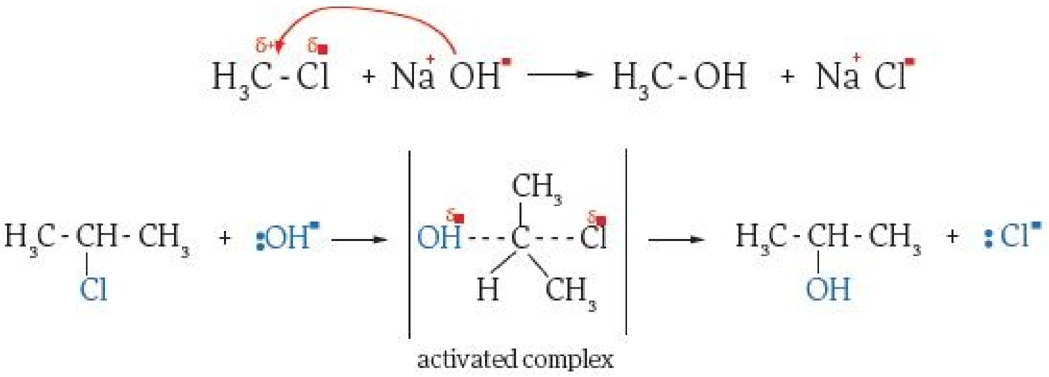
Chemical properties of haloalkanes

The reactivity of haloalkanes mainly depends on the polarizability of the C-X bond decreasing in the row: C-I > C-Br > C-Cl > C-F.

The chemical activity of haloalkanes can vary widely, depending on their structure.

Nucleophilic substitution of haloalkanes

For haloalkanes, nucleophilic substitution reactions (SN) are characteristic. This is due to the distribution of the electron density in the molecule. Chlorine shifts the electron density to itself due to higher electronegativity. A partial positive charge arises on the carbon atom. This electron-deficient carbon is an electrophilic center and can be attacked by some nucleophile. With the help of nucleophilic substitution reactions, it is possible to convert haloalkanes to alcohols, thiols, amines, and ethers. The general scheme of the nucleophilic substitution reaction can be represented as follows:



Under the action of a nucleophilic reagent (electron pair donor) OH-, a heterolytic disruption of the C-Cl polar bond occurs. The electron pair of this bond goes to the more electronegative atom Cl, which turns into the Cl- ion.

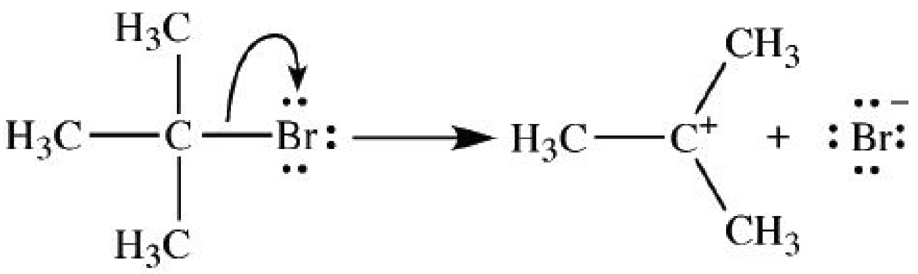
A new bond is formed due to the electron pair of the nucleophile (the nucleophile replaces the halogen in the halogenalkane molecule). The particle X- leaves, carrying electrons of the former σ-bond. This particle is called a "leaving group". Reactions of nucleophilic substitution are often reversible since any leaving group is also a nucleophile. To shift the equilibrium of the reaction to the right, a "good" nucleophile and a "good" leaving group are needed. A "good" nucleophile is an active nucleophile. How can we compare the strength of different nucleophiles?

1) Anions are more active nucleophiles than the corresponding neutral molecules because the anions are easier to give off electrons. For example, the OH- anion is a stronger nucleophile than the neutral H2O water molecule. Alcoholate/Alkoxide anion R-O- is more active than the molecule of alcohol R-OH, thiolate anion R-S- is more active than the molecule of thiol R-SH.

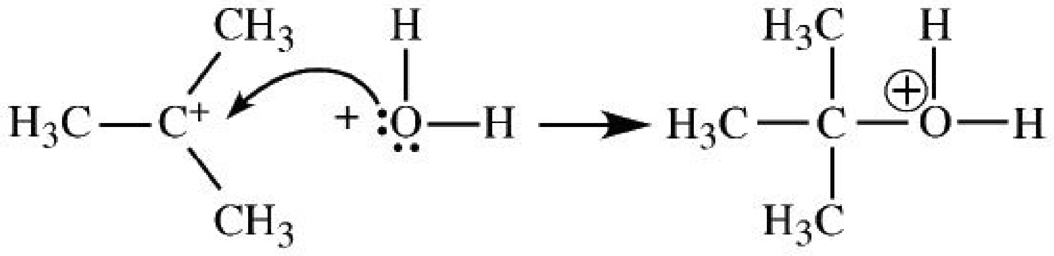
2) The lower the electronegativity of the atom of the nucleophilic center, the more active the nucleophile, such an atom more readily transfers the electron pair to the formation of a new σ-bond. Therefore, the ammonia molecule NH3 is a stronger nucleophile than the H2O water molecule (the electronegativity of nitrogen is lower than that of oxygen). A "good" leaving group, on the contrary, should be a weak nucleophile.

For example, a neutral water molecule is a better leaving group than a hydroxide anion. The halogen anions are "good" leaving groups due to the high electronegativity of the halogen atoms.

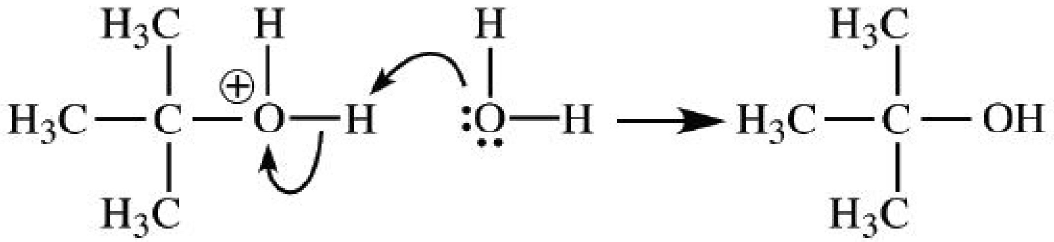
There are two types of nucleophilic substitution reactions by which haloalkanes react. They are called SN1 (substitution, nucleophilic, unimolecular) and SN2(substitution, nucleophilic, bimolecular). In case of SN1 reaction, reaction rate depends only on one molecule. For example, reaction of t-butylbromide with water occurs via SN1 mechanism. Rate of this reaction depends only on the concentration of haloalkane. Generally, substitution reactions with haloalkanes with tertiary carbon atom(bonded to halogen) occur via SN1 mechanism. In the first step, carbocation slowly forms by the ionization (dissocation) of a tert-butylbromide molecule (rate-limiting step).



The second step, water attacks the carbocation as long as it is formed.

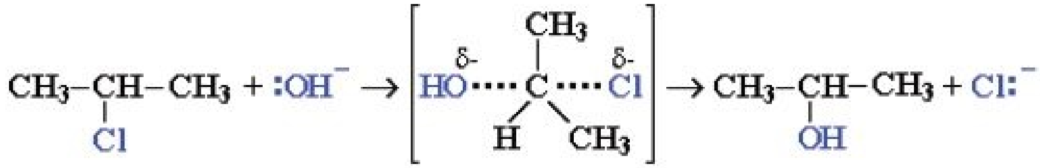


In the final step, water deprotonates protonated ethanol and forms ethanol.



In SN2 mechanism, nucleophile attacks the carbon atom to which a halogen atom is bonded. In order for this attack to happen, carbon atom has to be primary (or secondary). Because bulkiness around carbon atom hinders the attack of by a nucleophile. The SN2 mechanism is a one step mechanism, where a nucleophile attacks carbon atom (bonded to a halogen). As nucleophile - carbon bond is being formed, the carbonhalogen bond start to break. The transition state shown below, there is partial bond between nucleophile - carbon as well as halogen - carbon. Substitution reactions with primary carbon atom(bonded to halogen) proceeds with SN2 mechanism.

Substitution reactions of haloalkanes with secondary carbon atom(bonded to halogen) can occur both with SN1 and SN2 mechanism. However, the structure of an haloalkane, the strength of a nucleophile, and the condition of a reaction has to be taken account when determining the mechanism.



Nucleophilic substitution in general form:

$Y: + RX \rightarrow RY + X:$

Literacy

1. What happens when

- - ethyl bromide is treated with alcoholic KOH
- - methyl chloride is treated with alcoholic NaOH
- - methyl bromide is treated with aqueous KOH?

2. How following conversions can be carried out?

- - ethylene to ethanol
- - ethylene to butyne-1
- - ethane to butyne-1
- - ethane to ethanol
- - ethyl chloride to acethylene

3. Give the uses of freon, carbon tetrachloride, carbon trichloride, iodoform.

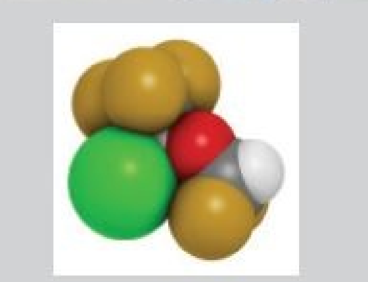
4. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides:

- - 2-chloro-propane
- - ethyl chloride

- - 2-chloro-butane
- - vinyl chloride

Chemfact

Halothane (CF3CHClBr) and Forane (CF2HOCClHCF3) are used in medicine as an anaesthetic.



Terminology

- nucleophiles - нуклеофильдер / нуклеофилы
- polarizability - полярлану /поляризуемость
- electrophilic - электрофильді/ электрофильный
- heterolytic disruption- гетеролитті бұзылу/ гетеролитическое разрушение

14.4 ELIMINATION REACTION OF HALOALKANES

How to synthesize acetylene from ethyl chloride?

You will:

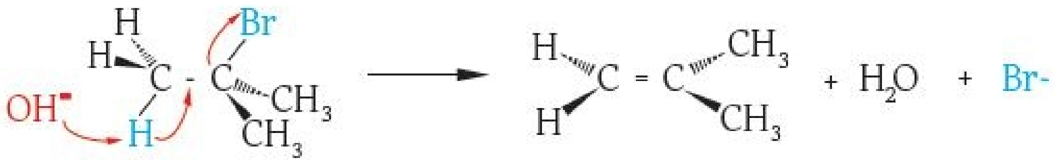
- explain the mechanism of the elimination reaction

Elimination reactions are accompanied by the elimination of halogenated hydrogen from the haloalkane and lead to the formation of alkenes. Elimination reactions (E) and nucleophilic substitution (SN) compete with each other, but under certain conditions, each of them can become dominant.

Elimination of one hydrogen atom from a haloalkane becomes the main process in the presence of nucleophilic reagents possessing high basicity. These include alcohol solutions of alkali metal hydroxides.

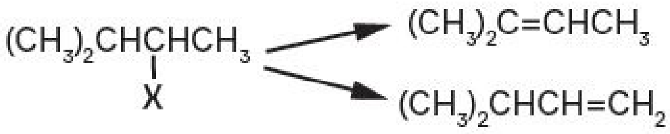
Increasing the temperature of the reaction mixture and the concentration of reagents also contribute to the elimination. Thus, when iodoethane is reacted with an aqueous solution of base, the main direction of the reaction is nucleic acid substitution, and the reaction product is ethyl alcohol. When an alcohol solution of a base is used, the elimination reaction becomes the dominant process and the reaction product is ethylene. The elimination reactions of haloalkanes can proceed along the monomolecular (El) and bimolecular (E2) mechanisms.

The mechanism of E2 (bimolecular elimination). Primary haloalkanes generally easily go to the elimination reaction according to the E2 mechanism. The elimination reaction proceeding along the bimolecular mechanism, which requires the presence of a base, goes in one step with the formation of a transition state, in which the molecules of two reagents participate in the formation. The rate of such reaction depends on the concentration of both reagents. The processes of breaking and formation of bonds in a transition state occur simultaneously.



Tertiary haloalkanes are most easily subjected to the elimination reaction. The reaction does not require a base as a reagent, but an ionizing solvent is necessary for its flow. The process is in two steps. The step determining the reaction rate is the formation of a carbocation. The second step involves the stabilization of the carbocation through the elimination of the proton.

The elimination reaction obeys Zaitsev's rule. So, the splitting off of the hydrogen atom in the elimination reactions occurs predominantly from the least hydrogenated carbon atom.



$$(CH_3)_2CH\underset{X}{\underset{|}{C}}HCH_3 \rightarrow (CH_3)_2C{=}CHCH_3$$

$$(CH_3)_2CH\underset{X}{\underset{|}{C}}HCH_3 \rightarrow (CH_3)_2CHCH{=}CH_2$$

The monomolecular mechanism of E1 is a two-step process. The ionization of the substrate with the formation of carbocation is ratedetermining step. In which carbocation quickly releases the proton to the base that is often used by the solvent:

Literacy

1. What happens when

- - ethyl bromide is treated with alcoholic KOH
- - methyl chloride is treated with alcoholic NaOH
- - methyl bromide is treated with aqueous KOH?

2. How following conversions can be carried out?

- - ethylene to ethanol
- - ethylene to butyne-1
- - ethane to butyne-1
- - ethane to ethanol
- - ethyl chloride to acethylene

3. Give the uses of freon, carbon tetrachloride, carbon trichloride, iodoform.

4. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides:

- - 2-chloro-propane
- - ethyl chloride
- - 2-chloro-butane
- - vinyl chloride

Chemfact

Haloalkanes used in organic synthesis as a reagent. For instance, in Fridel-Craft's reaction ethylchlorides or ethylbromides react with benzene to form benzene derivatives.

Terminology

- elimination - элиминирлеу /элиминация;
- simultaneous - бір уақытта /одновременное;
- carbocation - карбкатион /карбкатион.

QUESTIONS AND PROBLEMS

1. Draw the structures of all the structural isomers that have the molecular formula C4H9Br. Name each isomer according to IUPAC system.

2. Show all the possible structural formula of C3H7Cl.

3. Name the following halides according to IUPAC system:

- - CH3CH2CH(Cl)CH3
- - CH3CH2C(CH3)2CH2Cl
- - CH3CH(Br)CH2CH3
- - CH3CH2CH(Cl)CH3
- - (CH3)3CCH2Br
- - CH2=CH-Cl

4. Write the structures of the following organic halogen compounds.

- - 2-iodo-3-methylpentane
- - methylene chloride
- - chloroform
- - n-propyl fluoride
- - 1-bromopentane
- - 3-bromopentane
- - 1-chloro-2,2-dimethylpropane

5. 0.2 mole of an haloalkane weighs 30.8 g. Find its molecular formula.

6. How many grams of each of the constituent elements are contained in 0.6 mol of

- - carbon tetrachloride
- - bromoform
- - vinyl chloride?

How many atoms of each compound are contained in the same amount of compound?

7. Derive the empirical formula of a haloalkane that on analysis gave the following percentage composition: C=10%, H=0.88%, Cl=89.12%.

8. A compound gave a analysis the following percentage composition: C=39.74%, H=7.28%, Br=52.98%. Derive the molecular formula of the haloalkane.

9. Complete and balance the following reactions.

- - $CH3CH2CH2Br + NaOH \rightarrow$
- - $CH3CH2MgBr + HBr \rightarrow$
- - $CH3CH(Cl)CH2CH3 + KOH \rightarrow$

10. What is the molecular formula and the name of the hydrocarbon that is obtained from the reaction of 2-

chloropropane with an excess amount of sodium metal? Write out the reaction and explain.

11. What is the molecular formula of the hydrocarbon that is obtained from the reaction of 3-bromopentane with an excess amount of potassium metal? Write out the reaction.

12. Which alkyl halide pairs may be used to obtain 2–methylbutane?

13. What are the names of the compounds which are formed by the reaction of 2–bromopropane and 2–methyl–3–chlorobutane with a sufficient amount of Na?

14. What is the molecular weight of the compound that is produced by 2 moles of bromomethane and excess Na? Give its IUPAC name.

15. A scientist uses the chlorine Cl_2, in the synthesis of CCl_4 according to the given reaction equation

$4Cl_2 + CH_4 \rightarrow CCl_4 + 4HCl$

What mass of Cl_2 gas should be used to synthesis 96 g CCl_4? Assume that the yield of the reaction is 90%.

16. Find the mass of CH_3Br that is obtained from the CH_3OH that

takes up a volume of 13.44 L at STP. The yield of the reaction is 95%.

3CH3OH + PBr3 → 3CH3Br + H3PO4

17. What is the yield when 52 g of C2H4 reacts with Br2 solution to produce 300 g of C2H4Br2?

15
CHAPTER

ALCOHOLS

CHAPTER 15: ALCOHOLS

15.1 CLASSIFICATION OF ALCOHOLS

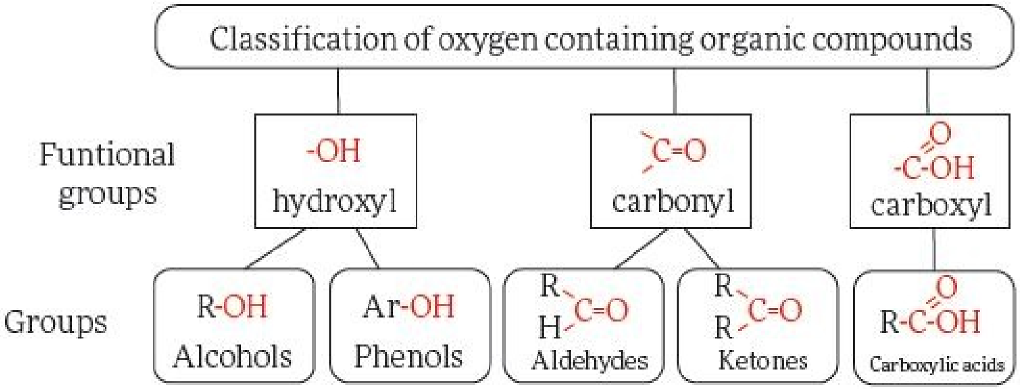
Fermentation of grape juice gives alcohol as a product. During exercise, our muscles also undergo fermentation and produce lactic acid. Why do not they produce alcohol?

You will:

- classify alcohols by the location of the functional group and by the number of hydroxyl groups

Oxygen containing organic compounds

There are a huge number of organic compounds, which, together with carbon and hydrogen, contain oxygen. They are called as oxygen containing organic compounds. The oxygen atom is contained in various functional groups that determine belonging of the compound to a particular class. Oxygen containing organic compounds include a large class of organic compounds: alcohols, phenols, aldehydes, ketones, carboxylic acids, ethers and esters, etc.



Classification of oxygen containing organic compounds

Alcohols

Alcohols are compounds that have a hydroxyl group (-OH) attached to a saturated carbon atom. Alcohols can be described as alkyl derivatives of water where one hydrogen in the water molecule replaced by an alkyl (R-) group. The general formula of alcohol is R-OH or CnH2n+1OH or CnH2n+2O.

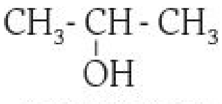
In the structure of alcohol carbon atom having the -OH group is attached to another carbon atom by a single bond and it is sp3 hybridized. The carbon chain of the rest of alcohol can be saturated or unsaturated. The saturated carbon atom having the -OH group may:

a) be a carbon atom of a simple alkyl group, as in the following examples

CH_3-OH

Methyl alcohol

cyclopentyl alcohol



$$\underset{\mid}{CH_3-CH-CH_3}$$
$$OH$$

isopropyl alcohol

b) be from an alkenyl or alkynyl group, or it may be a saturated carbon atom attached to a benzene ring as in the following examples.

$CH_2=CH-CH_2-OH$

propenyl alcohol

$CH\equiv C-CH_2-OH$

propynyl alcohol

benzyl alcohol

Classification of alcohols

ACCORDING TO THE NUMBER OF —OH GROUPS

Alcohols can be classified as monohydric and polyhydric alcohols according to the number of -OH groups in their structure

1 . Monohydric Alcohols

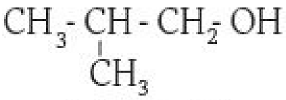
Alcohols containing only one hydroxyl group in their structure are called monohydric alcohols.

CH_3-OH

methyl alcohol

CH_3-CH_2-OH

ethyl alcohol

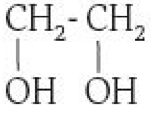


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$$

isobutyl alcohol

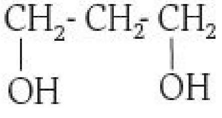
2. Polyhydric Alcohols

Alcohols containing two or more hydroxyl groups in their molecules are called polyhydric alcohols. Alcohols containing two -OH groups are called glycols or diols, and those with three -OH groups are called glycerols or triols.



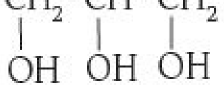
$$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

1,2-ethanediol
(glycol)



$$\underset{\displaystyle OH}{\underset{|}{CH_2}}-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

1,3-propanediol
(trimethylene glycol)



$$\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

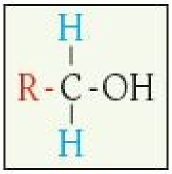
1,2,3-propanetriol
(glycerol)

ACCORDING TO THE CARBON ATOM HAVING THE -OH GROUP

Alcohols can be classified as primary, secondary and tertiary alcohols according to the condition of the carbon atom to which the hydroxyl group is attached.

Primary (1°) Alcohols

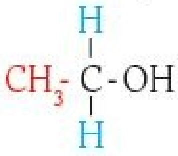
If the carbon bearing the -OH group is attached to only one other carbon, that carbon is said to be a primary carbon and the alcohol is a primary alcohol. Primary alcohols can be represented as:



$$\mathrm{R-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

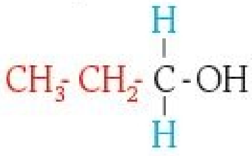
or $\mathrm{R-CH_2-OH}$

Some examples for primary alcohols are given below:



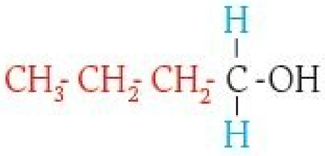
$$\mathrm{CH_3-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

ethyl alcohol



$$\mathrm{CH_3-CH_2-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

primary propyl alcohol

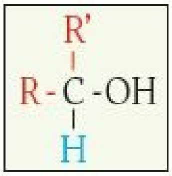


$$\mathrm{CH_3-CH_2-CH_2-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

primary butyl alcohol

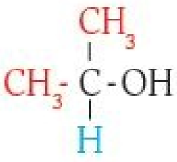
Secondary (2°) Alcohols

If the carbon with the -OH group is attached to two other carbon atoms it is called a secondary carbon and the alcohol is a secondary alcohol. An alcohol needs at least three carbon atoms to be secondary.



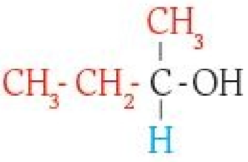
$$\mathrm{R-\overset{\displaystyle R'}{\underset{\displaystyle H}{C}}-OH}$$

secondary alcohol



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-OH}$$

secondary propanol

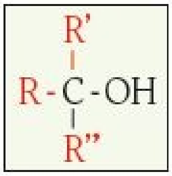


$$\mathrm{CH_3-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}-OH}$$

secondary butanol

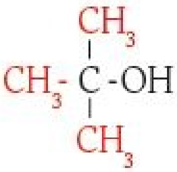
Tertiary (3°) Alcohols

If the carbon having the -OH group is attached to three other carbon atoms it is called a tertiary carbon, and the alcohol is tertiary alcohol. In a tertiary alcohol, there are at least four carbon atoms.



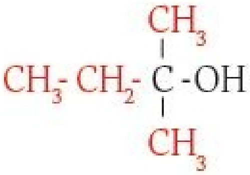
$R\text{-}\overset{R'}{\underset{R''}{C}}\text{-}OH$

tertiary alcohol



$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH$

tertiary butanol

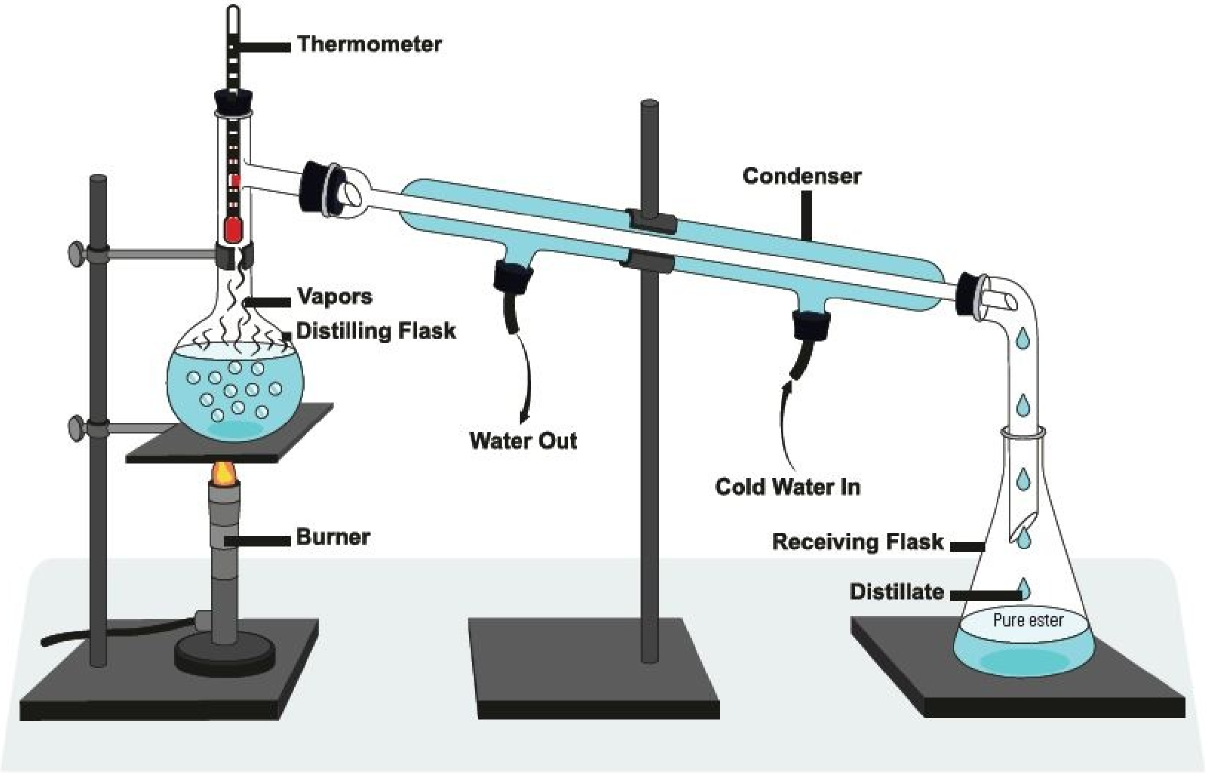


$CH_3\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}OH$

tertiary pentanol

Polyalcohols may be a combination of primary, secondary and tertiary depending on the positioning of each -OH group.

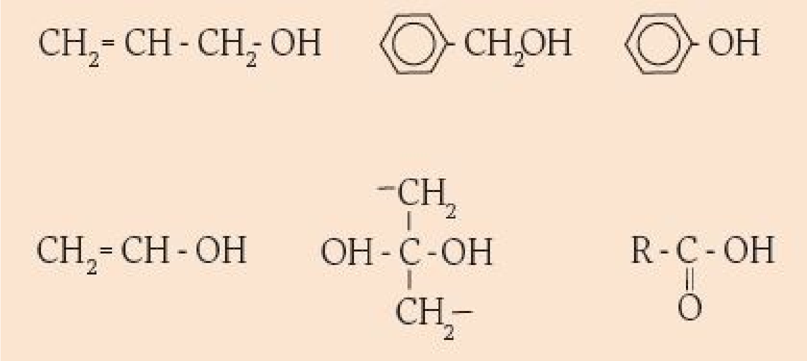
Fractional distillation is a method used to separate a mixture of miscible (for example alcohol and water) liquids



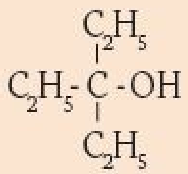
Separation of water from alcohol

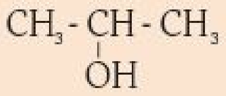
Literacy

1. Which of the followings are alcohols?

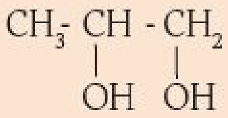


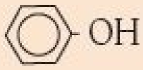
2. Classify the given alcohols as primary, secondary or tertiary.

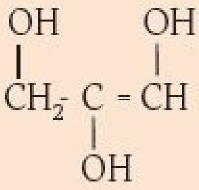

$C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{C}}-OH$

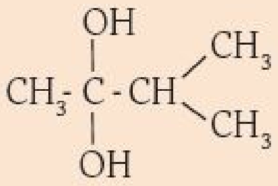

$CH_3-\underset{OH}{CH}-CH_3$

3. Which of the following is a polyhydric alcohol?

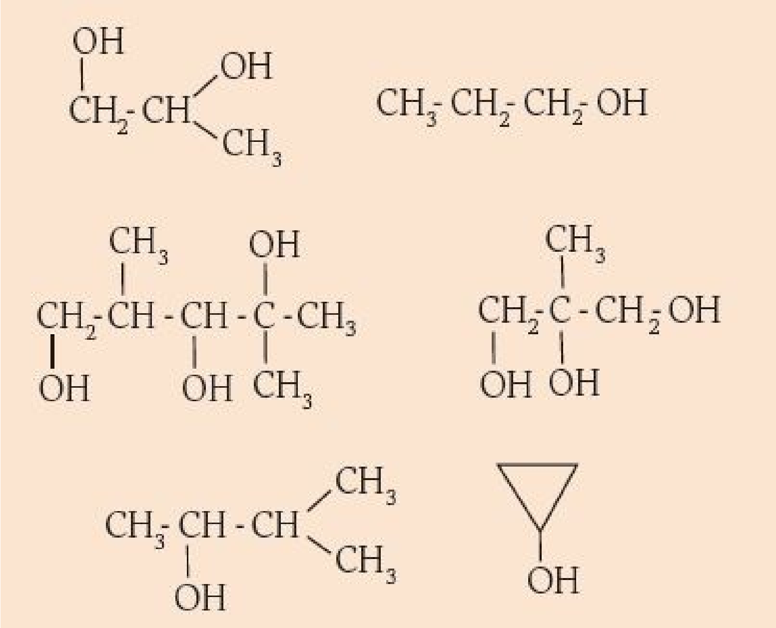

$CH_3-\underset{OH}{CH}-\underset{OH}{CH_2}$




$\overset{OH}{CH_2}-\underset{OH}{C}=\overset{OH}{CH}$



4. Which of the followings are tertiary alcohols?



Activity

Methyl alcohol is a one of the toxic substance. Its physical properties similar to ethanol. How to distinguish methanol from ethanol? Write a short plan describing this process. Use the internet and chemistry books to help you. Include the following information:

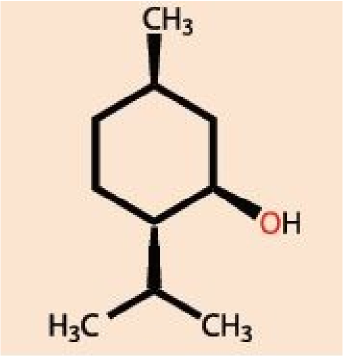
- - usage area of methanol
- - how to produce methanol in industry?

Chemfact

Ethanol is first organic compound synthesized by human (4000 years ago)

Chemistry around us

Menthol is a natural aromatic alcohol, obtained from mint.



Terminology

- primary - алғашқы /первичный;
- secondary - екінші /вторичный;
- tertiary - үшінші /третичный.

15.2 PREPARATION OF ALCOHOLS

Why is ethanol an antidote for methanol poisoning?

You will:

- know preparation of alcohols;
- know preparation of ethyl alcohol in industry;
- evaluate the advantages and disadvantages of ethanol production;
- study the toxic effects of alcohols on the human body.

Preparation of ethyl alcohol (or wine alcohol) by fermentation of carbohydrates

The essence of fermentation is that one of the simplest sugars - glucose, obtained from starch, under the influence of yeast fungi, breaks down into ethyl alcohol and carbon dioxide. It has been established that the fermentation process is not caused by the microorganisms themselves, but by the enzymes released by them - zymases. Vegetable raw materials rich in starch such as potato tubers, grain grains, rice grains are usually used to produce ethyl alcohol.

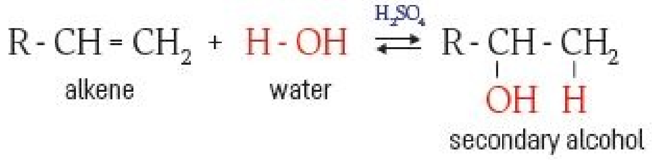
$$C_6H_{12}O_{6(s)} \rightarrow 2C_2H_5OH_{(l)} + 2CO_{2(g)}$$

Gasohol, common ethanol fuel mixtures made from sugarcane.

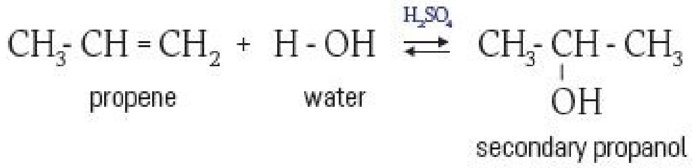
A bio-ethanol plant in Rotterdam, Netherlands

Synthesis of alcohols from alkenes

Alcohols can be prepared by the acid catalysed addition of water to alkenes. Concentrated H2SO4 is used as catalyst. The addition follows Markovnikov's rule. Secondary and tertiary alcohols can be produced by this method, but primary alcohols cannot (except for ethanol). This reaction is reversible.



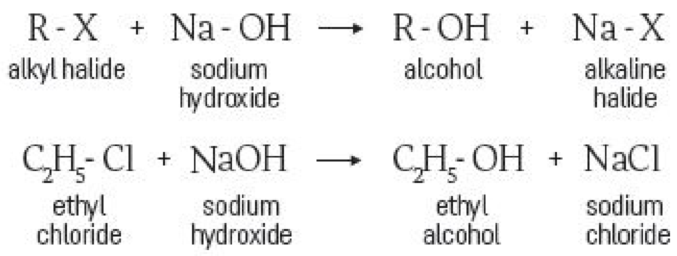
$$\underset{\text{alkene}}{R-CH=CH_2} + \underset{\text{water}}{H-OH} \xrightleftharpoons{H_2SO_4} \underset{\text{secondary alcohol}}{R-\underset{OH}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}}$$



$$\underset{\text{propene}}{CH_3-CH=CH_2} + \underset{\text{water}}{H-OH} \xrightleftharpoons{H_2SO_4} \underset{\text{secondary propanol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3}$$

Synthesis of alcohols from alkyl halides

Hydration of alkyl halides by solutions of alkalis produces alcohols. In this reaction the halogen atom is replaced by the -OH group to form an alcohol.

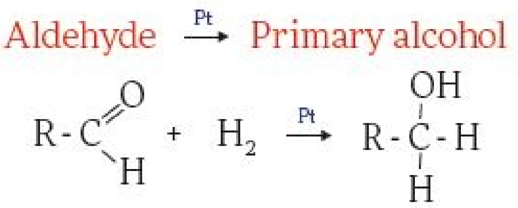


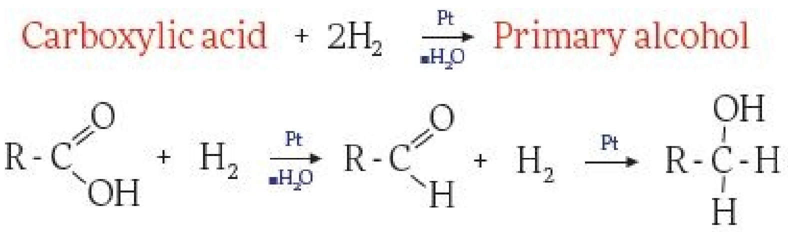
$$R\text{-}X + Na\text{-}OH \rightarrow R\text{-}OH + Na\text{-}X$$

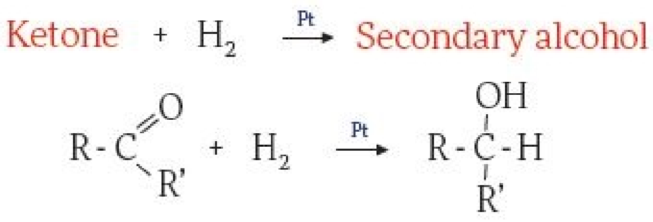
$$C_2H_5\text{-}Cl + NaOH \rightarrow C_2H_5\text{-}OH + NaCl$$

Synthesis of alcohols by the reduction of aldehydes, ketons and carboxylic acids

Alcohols can be obtained by reacting of aldehydes, ketones or carboxylic acids with hydrogen gas in the presence of a platinum metal. As a result of the reduction of aldehydes by one degree and carboxylic acids by two degrees primary alcohols are obtained. Reduction of ketones by one degree produces secondary alcohols.



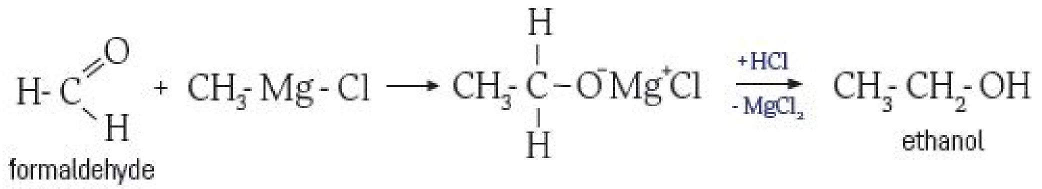




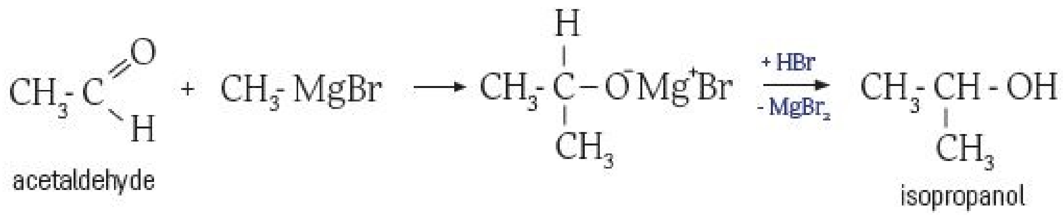
Synthesis of alcohols using Grignard reagents

Grignard reagents, alkyl magnesium halides (R – Mg – X) react with aldehydes and ketones. The Grignard reagent reduces these compounds, which contain the carbonyl group - C = O , to alcohols.

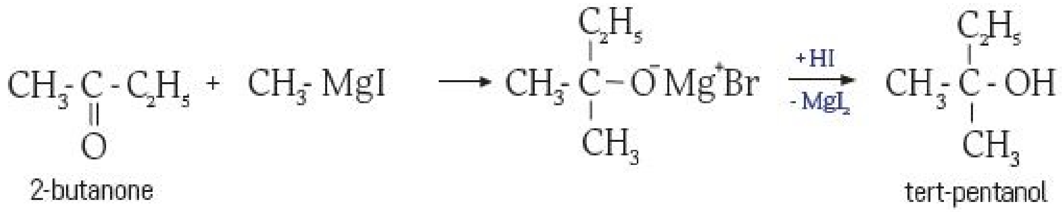
I. If a primary alcohol is desired, the reaction should be initiated with formaldehyde. By this way, an alcohol, containing at least two carbons, is produced.



II. If a secondary alcohol is desired, Grignard reagents should be reacted with an aldehyde other than formaldehyde.



III. If a tertiary alcohol is desired the Grignard reagent should be reacted with a ketone.



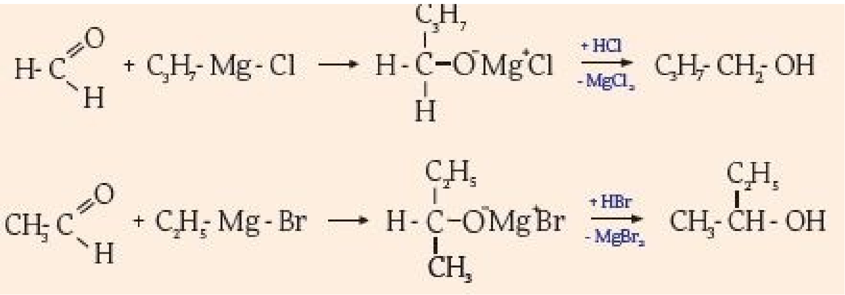
Example 1

Give the required reactants needed to produce the following compounds using Grignard reagents and write down the chemical equations.

a. 1-butanol

b. 2-butanol

Answer



Preparation of alcohols in industry

Ethyl alcohol by volume of production ranks first among all other organic products. It is widely used as a solvent and as a starting compound for various synthesises. Especially large amounts of ethyl alcohol are consumed in the production of synthetic rubber.

There are 2 main ways of producing ethanol in industry - biological (alcohol fermentation) and synthetic (hydration of ethylene).

1. Alcohol fermentation

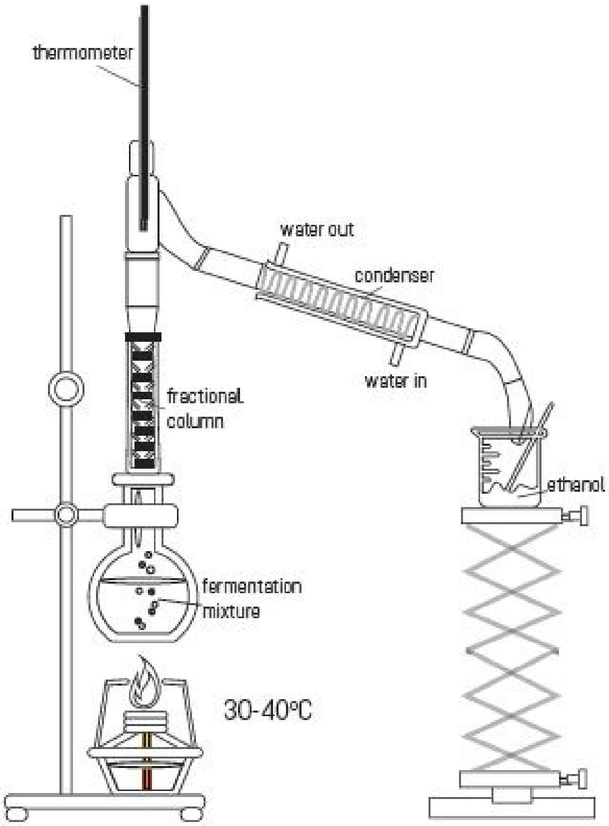
Biological method - fermentation of organic substances, containing carbohydrates (grapes, fruits) under the action of yeast and bacteria enzymes. In industry, instead of grape sugar, potato starch, cereals, sugar plant waste are used. Starch is preliminarily saccharified under the action of a special enzyme -

diastase, found in malt. Sugaring proceeds with the addition of water to the starch; thus forming a disaccharide - maltose $C_{12}H_{22}O_{11}$. Hydrolysis of maltose gives two molecules of glucose. Then the glucose is split into alcohol and carbon dioxide.

Fermentation of the pulp from berries

Sugarcane juice fermentation

Fermentation of sugarcane



Ethanol synthesis in the laboratory

The solution obtained as a result of fermentation contains no more than 15% ethanol, since in more concentrated solutions yeast is not viable. The ethanol thus obtained needs to be purified and concentrated, usually by distillation.

2. Hydration of ethylene

In industry, along with the first method, hydration of ethylene is used.

Hydration is possible in two ways:

a. direct hydration at a temperature of 300°C, pressure 7 MPa, orthophosphoric acid applied to silica gel, activated carbon or asbestos is used as a catalyst:

$$CH_2{=}CH_2 + H_2O \rightarrow C_2H_5OH.$$

b. hydration through the intermediate sulfuric acid ester stage, followed by its hydrolysis (at a temperature of 80 - 90°C and a pressure of 3.5 MPa):

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow CH_3\text{-}CH_2\text{-}OSO_2OH \text{ (ethyl sulfuric acid)}$$

$$CH_3\text{-}CH_2\text{-}OSO_2OH + H_2O \rightarrow C_2H_5OH + H_2SO_4$$

Activity

Write a description of the effects and harm of alcohol on the human body. Use the internet to help you. Include the following information:

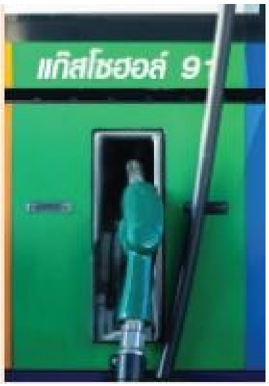
- - alcohol's effects on the body
- - how to treat for alcoholism?
- - what social and economic problems are linked to alcohol use?

Chemfact

Potassium dichromate used in alcohol testing. The oxidation of ethyl alcohol with orange K2Cr2O7 to form acetic acid and green Cr3+ is main indicator containing alcohol in human body.

Chemistry around us

Gasohol (also called E–10 Unleaded) contains 10% ethanol.



Demonstration №1

Preparation of ethyl alcohol by fermentation of glucose

Materials:

50 g of granulated sugar, water, porcelain cup, 10 g of yeast, flask, porcelain cup, gas tube.

Procedure:

1. Pour 50 g of granulated sugar and 200 ml of water in a flask. Shake the flask several times until the sugar dissolves.

2. Put 10 g of fresh yeast in porcelain cup. Add 50 ml of water. Stir the mixture.

3. Add mixture from porcelain cup into flask with sugar and water. Shake the mixture.

4. Close the flask with the gas tube inserted.

5. Place the flask in a warm place with a temperature of at least 25°C.

6. After 3-4 days you may proceed to distillation of alcohol.

In the process of fermentation, a double reaction occurs. First, sucrose hydrolyzes, passing into glucose and fructose, and then the glucose is split into alcohol and carbon dioxide.

Questions:

Write equations of all chemical reactions in the equations.

Literacy

1. Look at the picture at the beginning of the chapter. What do you understand from it? What are the other damages of alcoholic beverage?

2. What is the aim of ethanol production in Rotterdam's plant in Netherlands (picture above). What are the other advantages of ethanol production?

Terminology

- malt - уыт / солод;
- preliminarily - алдын ала /предварительно;
- viable - тіршілікке икемді /жизнеспособный;
- cereals - астық тұқымдастар/ злаки.

15.3 CHEMICAL PROPERTIES OF ALCOHOLS

How to distinguish ethyl alcohol from methyl alcohol?

You will:

- know chemical properties of alcohols

The chemical properties of alcohols are determined by the oxygen atom in the OH group. This oxygen atom is bonded to a carbon and hydrogen atom by sigma (single) bonds. The bonds between C-O and O-H are polar. The electronegativities of oxygen, carbon and hydrogen are 3.5, 2.5 and 2.1 respectively, oxygen having the highest electronegativity. When the polarities of C-O and O-H bonds are compared, it is seen that the O-H bond is more polar than the C-O bond. The hydrogen atom in the O-H bond becomes partially positively charged and therefore in some reactions, alcohols can act as proton (H+) donors. From primary alcohols to tertiary alcohols the polarity and therefore the proton donating ability of the O-H bond decreases.

Chemical properties of alcohols can be classified in two ways:

1. REACTIONS OF ALCOHOL INVOLVING O-H BOND BREAKAGE

Pure alcohols can undergo self-ionization in the same way as water but the ionization of pure alcohols is less than that of water. During the ionization, an alcohol molecule is converted into an alkoxide (RO-) ion by when it loses a proton, the molecule accepting the proton is converted into an oxonium ion.

$$\underset{\text{alcohol}}{R-O-H} + \underset{\text{alcohol}}{R-O-H} \leftrightarrow \underset{\text{oxonium ion}}{R-O^{+}-H} + \underset{\text{alkoxide ion}}{R-O^{-}}$$

$$\underset{\text{methanol}}{CH_3OH} + \underset{\text{methanol}}{CH_3OH} \leftrightarrow CH_3O^{+}H_2 + \underset{\text{methoxide}}{CH_3O^{-}}$$

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{ethanol}}{C_2H_5OH} \leftrightarrow C_2H_5O^{+}H_2 + \underset{\text{ethoxide}}{C_2H_5O^{-}}$$

The ionization percentage of alcohols decreases as the number of carbon atoms increases. In reactions with alcohols involving O-H bond breakage, protons (H+) are donated.

Reactions of alcohols with alkali metals

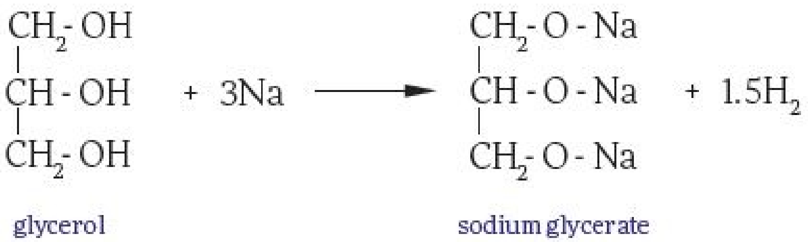
Alcohols display the properties of weak acids. The reactions of alcohols with active metals (such as Na and K) are slower than the equivalent reactions with water. During these reactions, basic salts of the alkoxide ion (RO-) are produced.

$$\underset{\text{alcohol}}{R\text{-}O\text{-}H} + Na \xrightarrow{\text{slow}} \underset{\text{sodium alkoxide}}{R\text{-}O^{-}Na^{+}} + 0.5H_2$$

$$\underset{\text{water}}{H\text{-}O\text{-}H} + Na \xrightarrow{\text{fast}} \underset{\text{sodium hydroxide}}{H\text{-}O^{-}Na^{+}} + 0.5H_2$$

Methanol and ethanol react strongly with Na and K. When the carbon chain of the alcohol extends the intensity of the reaction decreases. Generally, potassium is preferred for the long-chained alcohol reactions. Some metals, such as magnesium and aluminum can react with alcohols to produce H2 gas when their oxide layers are cleaned from their surfaces.

$$2CH_3CH_2OH + 2Na \rightarrow CH_3CH_2ONa + H_2$$



$$\begin{array}{l}CH_2-OH\\ |\\ CH-OH\\ |\\ CH_2-OH\end{array} + 3Na \longrightarrow \begin{array}{l}CH_2-O-Na\\ |\\ CH-O-Na\\ |\\ CH_2-O-Na\end{array} + 1.5H_2$$

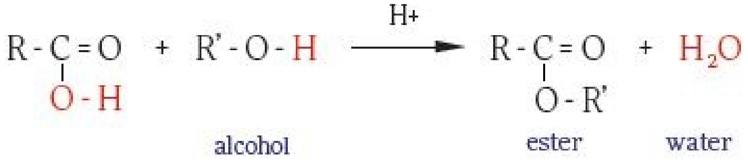
The rate of reaction of alcohols with alkali metals decreases from primary alcohols to tertiary alcohols. Basic alkoxides react with water (hydrolyze) to produce their initial alcohols.

$$\underset{\text{alkoxide}}{R-O^-Na^+} + \underset{\text{water}}{H-OH} \leftrightarrow \underset{\text{alcohol}}{R-OH} + NaOH$$

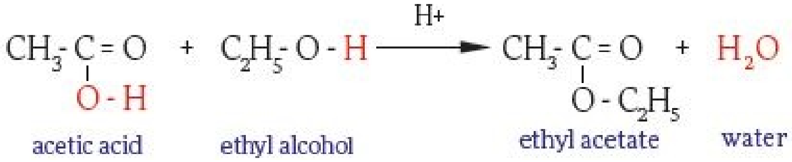
$$\underset{\text{sodium propylate}}{C_3H_7-O^-Na^+} + \underset{\text{water}}{H-OH} \leftrightarrow \underset{\text{propyl alcohol}}{C_3H_7-OH} + NaOH$$

Esterification Reactions

Reaction between alcohols and carboxylic acids give esters and water. This reaction is called esterification. In this reaction, the hydrogen atom from the OH group of an alcohol is replaced by the acyl group from a carboxylic acid. These reactions occur in the presence of strong acid catalysts such as HCl or H2SO4.



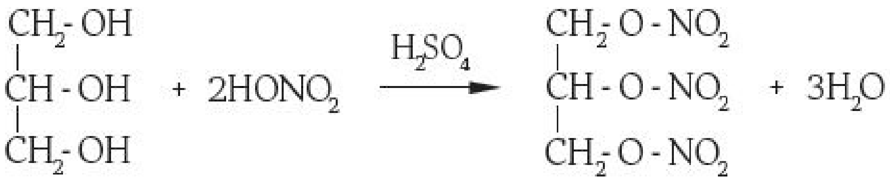
$$R-\underset{\displaystyle O-H}{\underset{|}{C}}=O + \underset{\text{alcohol}}{R'-O-H} \xrightarrow{H+} \underset{\text{ester}}{R-\underset{\displaystyle O-R'}{\underset{|}{C}}=O} + \underset{\text{water}}{H_2O}$$



$$\underset{\text{acetic acid}}{CH_3-\underset{\displaystyle O-H}{\underset{|}{C}}=O} + \underset{\text{ethyl alcohol}}{C_2H_5-O-H} \xrightarrow{H+} \underset{\text{ethyl acetate}}{CH_3-\underset{\displaystyle O-C_2H_5}{\underset{|}{C}}=O} + \underset{\text{water}}{H_2O}$$

Inorganic acids also react with alcohols to form esters. In these esterification reactions, as well as HNO3, H2SO4 and H3PO4, inorganic acid halides such as SOCl2 and PCl3 can be used.

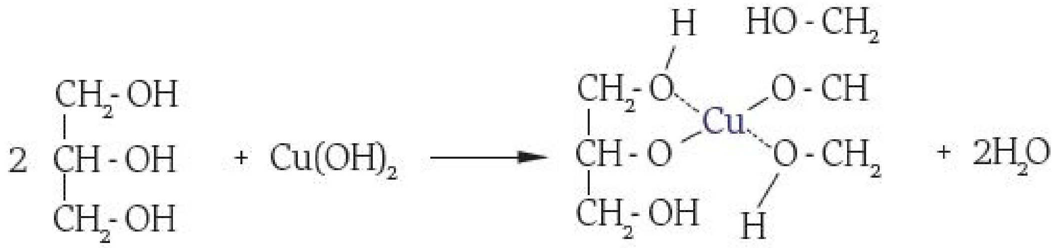
$$\underset{\text{nitric acid}}{HONO_2} + \underset{\text{alcohol}}{R\text{-}OH} \rightarrow \underset{\text{ester}}{R\text{-}O\text{-}NO_2} + \underset{\text{water}}{H_2O}$$

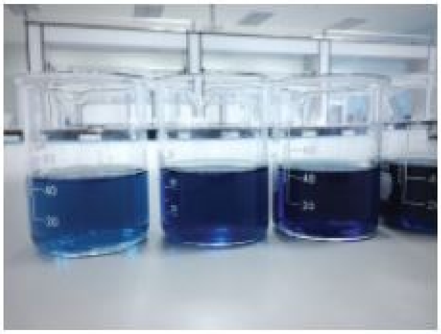


$$\begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array} + 2HONO_2 \xrightarrow{H_2SO_4} \begin{array}{l} CH_2\text{-}O\text{-}NO_2 \\ | \\ CH\text{-}O\text{-}NO_2 \\ | \\ CH_2\text{-}O\text{-}NO_2 \end{array} + 3H_2O$$

Qualitative reaction for polyhydric alcohols.

Reaction with copper (II) hydroxide in a basic solution is a qualitative reaction for polyhydric alcohols:





2. REACTIONS OF ALCOHOLS INVOLVING C-O BOND BREAKAGE

In alcohols it is seen that the R - C - OH structure has two lone pairs. These electrons cause alcohols to be protonated (accept protons) in acid solutions. In these type of reactions alcohols act as base.

During the reaction, the oxonium ion [R - C - OH]H+ is produced.

If this ion encounters a strong electrophile (a species attracted to electrons), a water molecule is removed from the ion as a result of C - O bond breakage.

Reactions of Alcohols with Hydrogen Halides

Alcohols react with hydrogen halides to produce alkyl halides. In these reactions, the OH group of the alcohol is replaced by the halide ion of the acid. All alcohols react with concentrated HBr and HI solutions to produce alkyl bromide and alkyl iodide. These reactions occur by a specific mechanism as shown below.

$$ROH + HX \rightarrow RX + H_2O \ (X=Br, I)$$

$$C_2H_5OH + HI \rightarrow C_2H_5I + H_2O$$

Concentrated HCl solution reacts with tertiary alcohols directly. But reacts with primary and secondary alcohols only in the presence of a ZnCl2 catalyst. A solution of ZnCl2 salt in HCl is known as “Lucas reagent”.

$$R\text{-}CH_2\text{-}OH + HCl \xrightarrow{ZnCl_2} R\text{-}CH_2\text{-}Cl + H_2O$$

$$(CH_3)_3C\text{-}OH + HCl \rightarrow (CH_3)_3C\text{-}Cl + H_2O$$

$$(CH_3)_2CH\text{-}OH + HCl \xrightarrow{ZnCl_2} (CH_3)_2CH\text{-}Cl + H_2O$$

$$CH_3\text{-}CH_2\text{-}OH + HCl \xrightarrow{ZnCl_2} CH_3\text{-}CH_2\text{-}Cl + H_2O$$

Dehydration of Alcohols

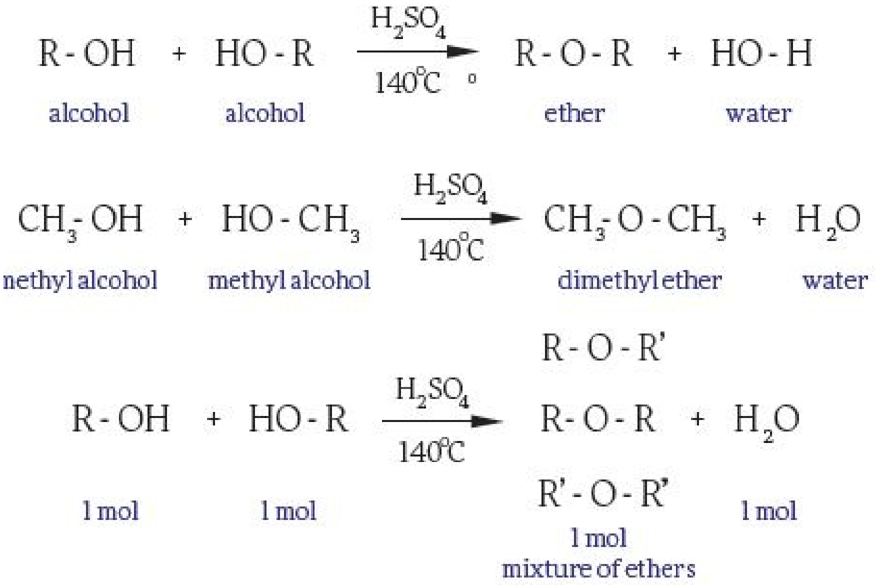
1. When one mole of monohydric alcohol is heated in the presence of a concentrated H2SO4 catalyst at high temperature, one mole of water and one mole of alkene is produced. To undergo this reaction, the carbon adjacent to the carbon with the OH group needs hydrogen atom bonded to it.

$$R\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{H_2SO_4\ t\,^0C} R\text{-}CH{=}CH_2 + H_2O$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{H_2SO_4\ t\,^0C} CH_3\text{-}CH{=}CH_2 + H_2O$$

The reaction follows Markovnikov’s rule.

2. At a lower temperature, a simple ether can be produced from the dehydration of two moles of monohydric alcohols.



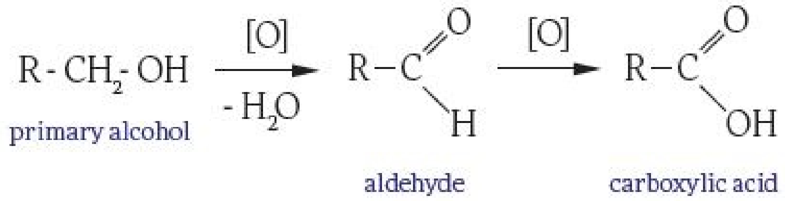
$$R\text{-}OH + HO\text{-}R \xrightarrow[140^0C]{H_2SO_4} R\text{-}O\text{-}R + HO\text{-}H$$

$$CH_3\text{-}OH + HO\text{-}CH_3 \xrightarrow[140^0C]{H_2SO_4} CH_3\text{-}O\text{-}CH_3 + H_2O$$

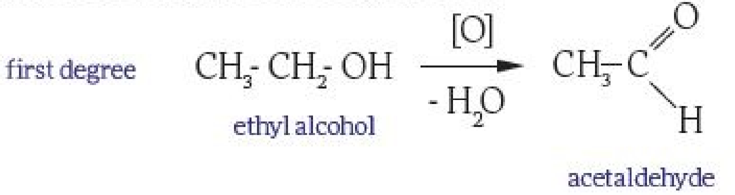
$$R\text{-}OH + HO\text{-}R \xrightarrow[140^0C]{H_2SO_4} \begin{matrix} R\text{-}O\text{-}R' \\ R\text{-}O\text{-}R \\ R'\text{-}O\text{-}R' \end{matrix} + H_2O$$

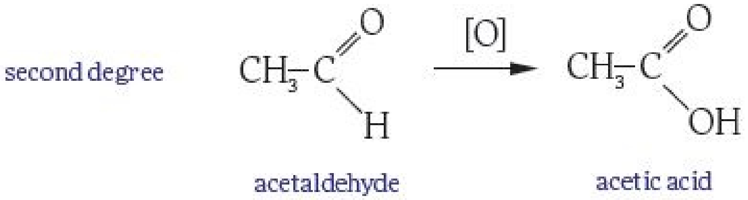
Oxidation of Primary Alcohols

In primary alcohols, the carbon atom bearing the -OH group has two hydrogen atoms, except methanol, which has three. Therefore, primary alcohols can be oxidized by two degrees. In the first oxidation, an aldehyde is produced, second oxidation gives a carboxylic acid.



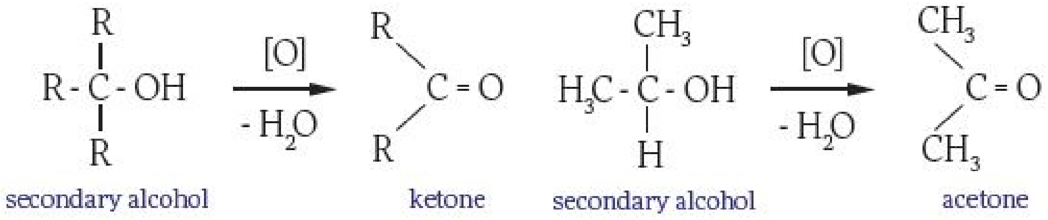
Let's examine the oxidation of ethyl alcohol.





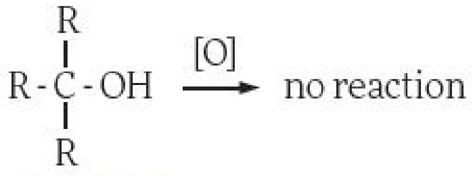
Oxidation of Secondary Alcohols

In secondary alcohols, there is only one hydrogen atom on the carbon atom bearing the OH group. Therefore, secondary alcohols can be oxidized by only one degree. The product of the oxidation is a ketone.



Oxidation of Tertiary Alcohols

Tertiary alcohols cannot be oxidized because they do not have a hydrogen atom on the carbon atom bearing the OH group.



$$R_3C\text{-}OH \xrightarrow{[O]} \text{no reaction}$$

tertiary alcohol

However, if tertiary alcohols are heated up to very high temperatures in the presence of a catalyst, they can decompose into unsaturated hydrocarbons and water.

Combustion reactions of alcohols

Alcohols, like hydrocarbons, burn in excess oxygen to form CO2 and H2O. Combustion reactions of monohydric, dihydric and trihydric alcohols are given below.

Monohydric alcohol:

$$C_nH_{2n+1}(OH) + 1.5nO_2 \rightarrow nCO_2 + (n+1)H_2O$$
$$C_3H_7(OH) + 4.5O_2 \rightarrow 3CO_2 + 4H_2O$$

Dihydric alcohol:

$$C_nH_{2n}(OH)_2 + (3n\text{-}1)/2O_2 \rightarrow nCO_2 + (n+1)H_2O$$
$$C_2H_4(OH)_2 + 2.5O_2 \rightarrow 2CO_2 + 3H_2O$$

Trihydric alcohol:

$$C_nH_{2n\text{-}1}(OH)_3 + (3n\text{-}2)/2O_2 \rightarrow nCO_2 + (n+1)H_2O$$
$$C_4H_7(OH)_3 + 5O_2 \rightarrow 4CO_2 + 5H_2O$$

Example

A member of the diatomic alcohols reacts with excess sodium metal to produce 37 grams of an alkoxide and 5.6 L of H2 gas at STP. Find the molecular formula of the alcohol.

Solution

The general reaction of diatomic alcohols with Na metal:

CnH2n+2O2 + 2Na → CnH2n(ONa)2 + H2

n(H2) = 5.6 L / 22.4 L/mol = 0.25 mol of H2 gas is produced.

According to the equation 1 mol H2 is produced with 1 mol alkoxide compound. So the number of moles of alkoxide is 0.25 mol.

M of alkoxide is = m / n = 37 / 0.25 = 148 g/mol

CnH2n(ONa)2 = 148 g/mol , 12n + (2n × 1) + (16 + 23) × 2 =148, n=5

The alkoxide compound has 5 carbon atoms.

The general formula of a dialcohol is CnH2n+2O2.

So the formula is C5H12O2

Activity

Write a description of the odors of esters. Use the internet to help you. Include the following information:

- - natural esters in a fruits
- - how to synthesis of esters in the lab

Chemfact

Methanol, CH3OH, is the fuel used in race cars

Chemfact

Glycerin reacts with nitric acid to produce trinitroglycerin. Trinitroglycerin is explosive organic substance, main component of dynamite.

Chemistry around us

Addition of 5–30 % methyl alcohol to gasoline decreases polluting particles produced from car exhausts. Methyl alcohol can be produced from substances other than petroleum. The most important and the cheapest being coal. It can also be produced from wood, agricultural remnants and dumps.

Literacy

1. 40 grams of 92% pure (by mass) ethyl alcohol reacts with an excess amount of potassium metal. How many liters of H_2 gas

are produced at the end of the reaction at STP (impurities in the mixture do not react with potassium).

2. When 20 grams of an ethane - ethanol mixture is reacted with an excess amount of Na metal, 2.8 L of H_2 gas is produced at STP. What was the mass percentage of ethyl alcohol in the original mixture?

3. 1 mole of acetic acid (CH_3COOH) reacts with 1 mole of a monohydric alcohol to produce an ester with a molar mass of 102 g/mol. What is the molecular formula of the alcohol used in the reaction? [CH_3COOH : 60 g/mol, H_2O : 18 g/mol, H : 1 g/mol, C : 12 g/mol, O : 16 g/mol]

4. When a 115 gram sample of impure ethyl alcohol (C_2H_5OH) is reacted with an excess amount of acetic acid (CH_3COOH), 176 grams of ester is obtained. What is the mass percentage of pure alcohol in the sample? (C_2H_5OH : 46 g/mol, CH_3COOH : 60 g/mol)

5. Write the equations for the reactions between the following substances.

- a. 2–propanol + Lucas reagent;
- b. 2–methyl–2–butanol + HCl

6. Write the equations for the following reactions.

- a. Dehydration of n – butanol in the presence of a H_2SO_4 catalyst at 180°C.
- b. Dehydration of isopropanol in the presence of a H_2SO_4 catalyst at 140 °C.

7. A sample of 50 gram of 92% pure ethyl alcohol is used to produce ethylene with an 80% yield,

- a. How many grams of alkene can be obtained?
- b. How many grams of ether can be obtained?

(C_2H_5OH : 46 g/mol, $C_4H_{10}O$: 74 g/mol)

8. The molar mass of an aldehyde which is produced by the one degree oxidation of a monohydric alcohol is 46 g/mol. Calculate the molar mass of the alcohol used in this reaction.

9. A 10 grams mixture of 2-methyl-2-propanol and 2-butanol is reacted with excess $K_2Cr_2O_7$ in acidic solution. At the end of the reaction 3.6 grams of ketone is obtained. Find the percentage of 2-butanol in the original mixture.

10. When 0.25 mol of a monohydric alcohol is burned, 16.8 L of CO_2 gas is produced at STP. What is the molecular formula of the alcohol?

Terminology

- alkoxide - алкоксид

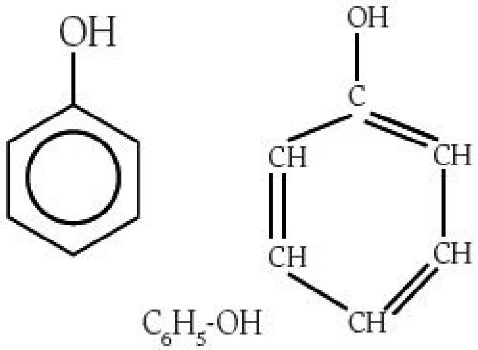
15.4 PHENOL AND ITS PROPERTIES

What is the distinguishing test between alcohol and phenol?

You will:

- know the composition and properties of phenol,
- know the practical use of phenol for plastic synthesis.

Phenols are compounds that have the general formula Ar–OH (C6H5-OH). In phenols, the carbon atom to which the –OH group is attached undergoes sp2 hybridization, so in general, phenols display different properties to alcohols.



C_6H_5-OH
phenol

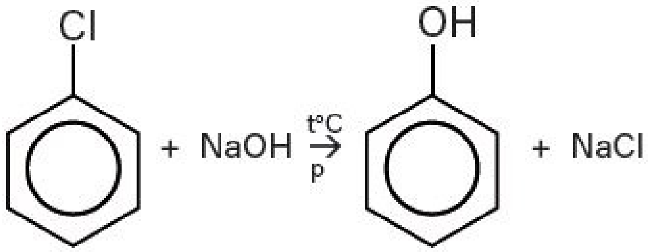
Physical properties

Pure phenol is a colorless, crystalline solid with a melting point of 43°C. It is hydrated and turns red when exposed to air. It is soluble in water, like alcohols and ethers. Phenol is a poisonous substance and contact with skin causes burns. Dilute solutions of phenol are used as antiseptics and disinfectants.

Phenol is widely used as a starting material in the manufacture of nylon, plastics, dye stuffs, aspirin and antiseptics.

Preparation

In industry, phenol is obtained from coke by distillation though there are various ways of manufacturing phenol in laboratories. Chlorobenzene reacts with NaOH under high temperature and pressure to produce phenol.



Chemical properties

Phenol is more acidic than alcohols (but less acidic than carboxylic acids). Aqueous solutions of phenol are weakly acidic and turn blue litmus slightly to red.

R-OH < C6H5-OH < R-COOH

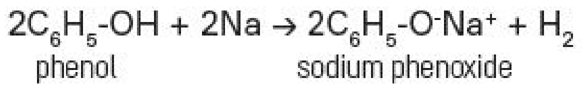
1. Phenol reacts with NaOH like carboxylic acids whereas alcohols do not

$$\underset{\text{phenol}}{C_6H_5\text{-}OH} + NaOH \rightarrow \underset{\text{sodium phenoxide}}{C_6H_5\text{-}O^-Na^+} + H_2O$$

2. Phenol does not react with basic salts such as NaHCO3 like alcohols.

C6H5-OH + NaHCO3 → no reaction

3. Phenol reacts with Na metal to form phenoxide salt after heating:

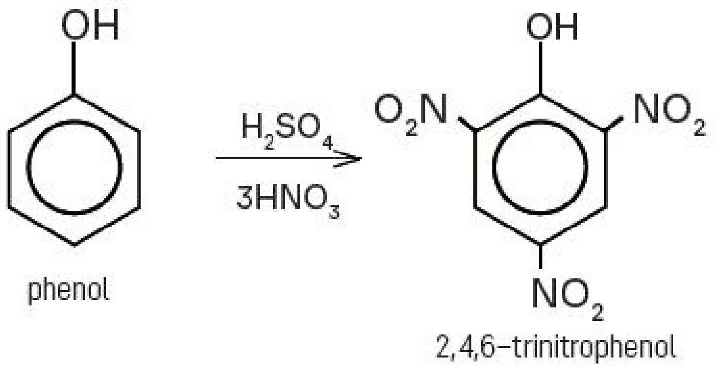


$$\underset{\text{phenol}}{2C_6H_5\text{-}OH} + 2Na \rightarrow \underset{\text{sodium phenoxide}}{2C_6H_5\text{-}O^-Na^+} + H_2$$

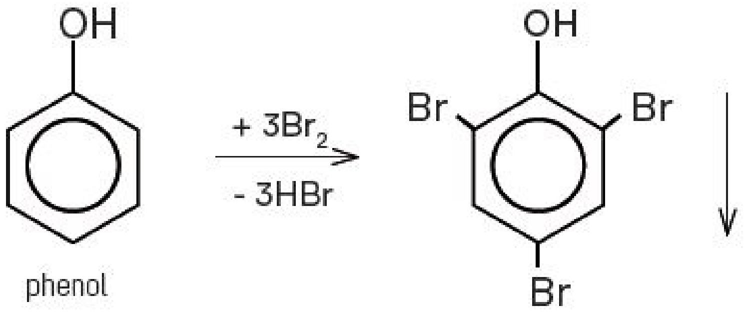
4. Phenol burns in a plentiful supply of oxygen to give carbon dioxide and water.

C6H5-OH + 7O2 → 6CO2 + 3H2O

5. Phenol is converted into 2,4,6–trinitrophenol by concentrated nitric acid in the presence of H2SO4 catalyst.



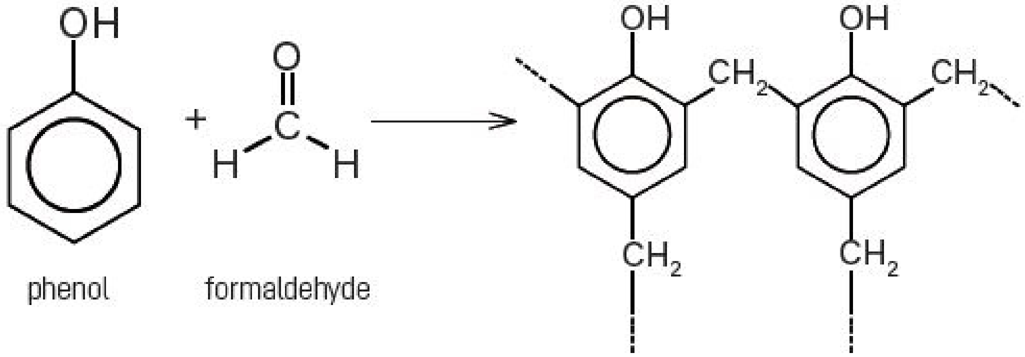
6. Phenol can be halogenated by halogens in their aqueous solutions



phenol

2,4,6-tribromophenol
white precipitate

7. The most important reaction of phenol is its polycondensation reaction with formaldehyde, which produces phenolic resins (PF).



phenol

formaldehyde

phenol formaldehyde resin

Chemfact

Phenol is the raw material for the production of many substances, ranging from aspirin to plastics.

Chemistry around us

Electrical insulators are made from phenolic resins because of its insulating and heat resistant properties.

Literacy

1. Phenols are more acidic than alcohol? Why?

2. What mass of 2,4,6–tribromophenol can be produced from 80 grams phenol with 60% efficiency?

3. Why is phenol not soluble in NaHCO3?

4. Phenol formaldehyde used in electrical appliances. Why?

QUESTIONS AND PROBLEMS

1. Determine the molecular mass for

- - methyl alcohol
- - ethyl alcohol
- - isopropanol
- - pentan-1-ol

2. How many grams of each of the constituent elements are contained in 0.6 mol of

- - methanol
- - glycerine
- - ethanol?

How many atoms of each compound are contained in the same amount of compound?

3. What is the mass of one molecule of C2H5OH, CH3OH?

4. Derive the empirical formula of a alcohol that on analysis gave the following percentage composition: C=60%, H=13.33%, O=26.67%.

5. A compound gave a analysis the following percentage composition: C=68.18%, H=13.64%, O=18.18%. Derive the molecular formula of the compound.

6. Derive the empirical formula of a alcohol that on analysis gave the following percentage composition: C=39.13%, H=8.7%, O=52.17%.

7. A 50 g sample of an organic compound was combusted in a oxygen to yield 110 g CO2 and 180 g H2O. If the original compound contained only C, H, and O, what is its empirical formula?

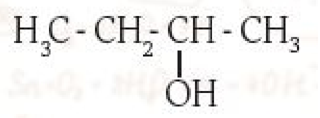
8. A 4.8 g sample of an organic compound was combusted in a oxygen to yield 3.36 L CO2 and 5.4 g H2O. Relative density of this organic compound according to hydrogen gas is 16. If the original compound contains only C, H, and O, what is its empirical formula?

9. 100 ml of 92% pure (d=0.8 g/ml) ethyl alcohol reacts with an excess amount of sodium metal. How many liters of H2 gas are produced at the end of the reaction at STP?

10. 0.46 g of unknown alcohol reacts with an excess amount of sodium metal to produce 112 ml hydrogen gas. Find molecular formula of an alcohol.

11. A 2.3 g sample of an alcohol was combusted in a oxygen to yield 4.4 g CO2 and 2.7 g H2O. Relative density of this organic compound according to air is 1.59. What is its molecular formula?

12. Give the common names of the following compounds.

- - CH_3CH_2OH
- - $CH_3CH_2CH_2OH$
- 
  $H_3C-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

13. Draw the structural formula of the following compounds.

- - 2,3–dimethyl–2,3–butanediol
- - 2,4–dimethyl–1–pentanol
- - 4–ethyl–2–pentanol

14. When 20 grams of an ethane - ethanol mixture is reacted with an excess amount of Na metal, 2.8 L of H_2 gas is produced at STP. What was the mass percentage of ethyl alcohol in the original mixture?

15. When 300 grams of a hexane-butanol mixture is reacted with an excess amount of potassium metal, 38.08 L of H_2 gas is produced at STP. What was the mass percentage of butyl alcohol in the original mixture?

16. Draw the structural formula of the isomers of C_4H_8O. Name all the compounds.

17. Write the structural formulas for the secondary alcohols $C_5H_{11}OH$.

18. Write the structural formulas for the C4H8(OH)2.

19. Write the equations for the reactions between propanol-1 and the given substances. Name the products.

- - Na
- - CH3COOH
- - HBr
- - C2H5OH (H+, to)

20. Write the equations for the reactions between ethyl alcohol and the given substances. Name the products.

- - K
- - O2 - CuO, to
- - C2H5OH (H+, to)

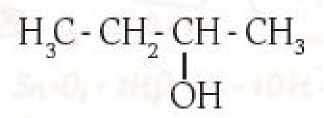
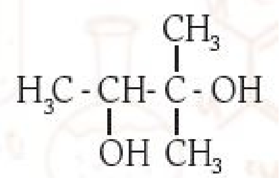
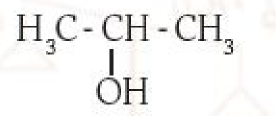
21. Ethylene gas obtained from 40 grams ethyl alcohol solution is saturated with 200 grams of Br2 solution, 5.6% by mass. What is the percentage purity of the ethyl alcohol solution?

22. Ethylene gas obtained from 100 grams ethyl alcohol solution is saturated with 100 grams of Br2 solution, 12% by mass. What is the percentage purity of the ethyl alcohol solution?

23. Explain Markovnikov's rule and complete the reactions below:

- - 4–bromo–3–heptene + H2O →
- - tert-butylethylene + H2O →
- - isoamylethlene
- - 2,3-dimethyl-2-pentene
- - 2,3-dimethyl-2-butene
- - propene
- - butylene
- - 3-methyl-1-butene
- - 3-methyl-1-pentene

24. Write the names and molecular formula of the alkenes obtained by the dehydration of the following alcohols with a H2SO4 catalyst:

- - CH3CH2OH
- 
  $H_3C-CH_2-\underset{OH}{CH}-CH_3$
- 
  $H_3C-\underset{OH}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-OH$
- 
  $H_3C-\underset{OH}{CH}-CH_3$

25. Write the structural formulae of the following compounds

- - 3-ethyl-3-methyl-2-pentanol
- - 2,2-dimethyl-1,4-hexandiol
- - 1,3-butandiol
- - 3-butene-1-ol
- - isopropyl alcohol
- - isobutyl alcohol

- - tert-pentanol
- - glycol
- - neo-pentanol
- - 3,3-dichlorocyclohexanol

26. Explain the primary, secondary and tertiary alcohol terms by giving an example of each.

27. Why do alcohols show both polar and nonpolar properties. Explain.

28. When 0.05 mol of a monoalcohol is burned, 2.2 grams of CO2 is produced. How many liters of oxygen gas are used at STP?

29. When 6.4 g of a monoalcohol is burned, 8.8 grams of CO2 is produced. How many liters of oxygen gas are used at STP?

30. When 27 g of a monoalcohol is burned, 30.24 L of CO2 is produced. How many liters of oxygen gas are used at STP?

31. If 5.4 grams of H2O is added to a sample of an alkene, 26.4 grams of a monoalcohol is obtained. What is the molecular formula of the alcohol?

32. If 27 grams of H2O is added to a sample of an alkene, 111

grams of a monoalcohol is obtained. What is the molecular formula of the alcohol?

33. 10 gram of 2-butanol is oxidised by an excess amount of acidic $KMnO_4$ solution and the reaction occurs with 74% efficiency. What is the mass and molecular formula of the substance produced?

34. If water is added to 2-butene, product A is obtained. At the end of the oxidation of A, compound B is obtained. Give the products A and B.

35. 6.3 grams of propylene reacts with water. The formed substance is added to an excess amount of $KMnO_4$ under heat and acidic media. How many grams of product is formed?

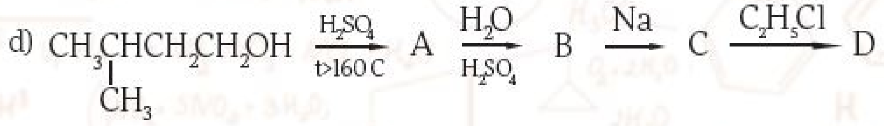
36. Write equations for each step of the given reaction chains.

a) butanol-1 $\xrightarrow{A}$ butene-1 $\xrightarrow{B}$ 2-chlorobutane $\xrightarrow{C}$ butene-2 $\xrightarrow{D}$

$\longrightarrow$ butandiol-2,3

$$\begin{tikzcd}
 & & & & & E \\
\text{b) } CH_3CH_3 \arrow[r, "Br_2", "h\nu"'] & A \arrow[r, "Na"] & B \arrow[r, "Br_2", "h\nu"'] & C \arrow[r, "H_2O", "t°C"'] & D \arrow[ur, "Na"] \arrow[dr, "CuO, t\,C"'] & \\
 & & & & & F
\end{tikzcd}$$

c) propanol-2 $\xrightarrow{HCl} A \xrightarrow{Na} B \xrightarrow[h\nu]{Br_2} C \xrightarrow[h\nu]{Br_2} D \xrightarrow[\text{aqueous solution}]{NaOH} E$



d) $CH_3CHCH_2CH_2OH$ with CH_3 below the second C: $CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_2OH \xrightarrow[t>160\,C]{H_2SO_4} A \xrightarrow[H_2SO_4]{H_2O} B \xrightarrow{Na} C \xrightarrow{C_2H_5Cl} D$

e) glucose $\xrightarrow{\text{fermentation}} A \xrightarrow{HCl} B \xrightarrow{Na} C \xrightarrow[h\nu]{Br_2} D \xrightarrow[\text{aqueous solution}]{NaOH} E \xrightarrow[t<140\,C]{H_2SO_4} F$

37. When 106 grams of a mixture of cyclopentanol and water reacts with excess Na, 44.8 L of H2 is produced at STP. Find the mole percentage (%) of cyclopentanol in the mixture.

38. When 15.6 grams of a mixture of methanol and ethanol reacts with excess oxygen, 13.44 L of CO2 is produced at STP. Find the mass percentage (%) of ethanol in the mixture.

39. When 16.5 grams of a mixture of methanol and ethanol reacts with excess oxygen, 26.4 g of CO2 is produced. Find the mass percentage (%) of methanol in the mixture.

40. In the 3 test tubes there are aqueous solutions of methanol, phenol, acetic acid. Describe how can you identify the solutions.

41. In the 2 beaker there are aqueous solutions of methanol and ethanol. Describe how can you identify the solutions.

ANSWERS

Chapter 1

2) a – 10.801,

b – 24.3202,

c – 93,

d – 79.9862

3) 56.5%, 43.5%

4) a – 10,

b – 90,

c – 96 ,

d – 10

Chapter 2. Periodicity

14) K > Na > Mg > C

34) CaO – basic, CO2, SiO2, SO3, SO2 - acidic

38) MnO, MnO2, Mn2O7, Mn(OH)2

Chapter 3. Chemical bonds

Double, triple bond formation

O2 - 1σ, 1π

SiO2 - 2σ, 2π

Ionic bond, ionic crystal networks

2) Li2O, KCl, MgI2

3) NaCl, CaI2, Li2S

5) ionic, covalent, covalent, ionic, covalent, ionic, covalent

8) nonelectrolyte, electrolyte, electrolyte, nonelectrolyte

10) BaI2, SrO, AlBr3, Cs2O

11) CaCl2, BaSO3, CaO

12) Na3PO4, Sr(NO3)2, Al2(SO4)3

Metallic bond, metallic crystal networks

5) ionic, covalent, metallic

Chapter 4. Stoichiometry

1) 2.42×1024 atom, 5.418×1023 atom, 4.4276×1024 atom

2) 0.98 mol, 21.927 mol, 7.26×10-3 mol

3) 7.75 g, 4.68 g

4) Aluminum

5) 0.1498 mol, 5 mol

6) 23 mol,

30 mol,

35 mol,

70 mol

7) 1906.3 g

8) 0.875 mol

9) 3.62 tonn

10) 4.16 g

11) 49.4 L

12) 729.73 g

13) 355.6 g, 48.375 g

14) 1613.8 g

15) 868.3 g

16) 6.4 kg, 152.73 g, 6 kg

17) 0.556 mol, 7.692 mol, 1.8 mol

18) I, III

19) 223.65

20) 70.7 g of KNO3

21) 32.4 g of water

22) 22.4 L of HCl

23) 3.36 L of NO

24)

- – O2, 360 g of water,
- 43.33 mol of C6H6 (excess)

- – 1.15 mol of CO2, 0.575 mol H2O

- – 15 mol CO_2, 7.5 mol of water

25) 102.458 g SF_6, F_2 is limited

26) 16.8 mol of oxygen

27) 6.8 g of ammonia

28) Ar(X)=1

29) Ar(X)=12

30) Ar(X)=12

31) 25.83 g of HI

32) 311.5 L of oxygen

33) 19.6 L of chlorine

34) 130.33 L of hydrogen

35) 0.747 L of NO

36) 2.08 L of N_2O

37) 3 L of nitrogen

38) 348.2 L $CaCO_3$

39) 127.4 g of ammonium dichromate

40) 114.64 L of NO_2, 57.32 L of O_2

41) 186.67 L of NO_2

42) 26.88 L of hydrogen

43) 31.77 L of SO_2

44) 57%

45) 88%

46) 86%

Chapter 5. Introduction to Thermodynamics

3) exothermic,

exothermic,

endothermic.

Endothermic

6) endothermic

7) exothermic, $\Delta H=-210$ kJ

Hess's law

1) $\Delta H=-113.7$ kJ

2) $\Delta H=277.4$ kJ, $\Delta H=-2032.4$ kJ

3) $\Delta H=211$ kJ

4) $\Delta Hr=-777.7$ kJ

5) $\Delta Hr=-890.29$ kJ

6) $\Delta Hr=-7791.32$ kJ

7) $\Delta H=-115.38$ kJ

Enthalpy

1) Q =2714 kJ

3) ΔHf(C_6H_6)=48.51 kJ

4) Q=314.8 kJ

Entropy

1) ΔSR=-306.5 J/K

ΔSR=-84.6 J/K

ΔSR=334.2 J/K

ΔSR=627 J/K

2) ΔSR=488.4 J/K

3) ΔSR=19.98 J/K

4) ΔSR=-175.83 J/K

Gibbs's energy

1) ΔG=-197.8 kJ

4) T=619 K

Chapter 6. Kinetics

1) 0.25 mol / (L×s)

2) 1.2×10^{-3} mol / (L×s)

3)

$r = k \times [H_2S] \times [SO_2]$

$r = k \times [Cl_2]$

$r = k \times [CO] \times [H_2O]$

4) t1/2 = 502 min

6) r(HCOOH) = + 0.02 mol / (L × s)

7) r(NO) = + 3.47 × 10-5 mol / (L × s)

r(H2O) = + 5.2 × 10-5 mol / (L × s)

8) third

Chapter 7. Equilibrium

3) Kc=Kp

Kc=Kp

4) Kp=Kc / RT

Kc=Kp

5) Kc=40, Kp=1.22

6) Kc=4.44, Kp=0.0061

7) Kc=4.32

8) [H2]=0.07 mol

[F2]=1.07 mol

[HF]=3.86 mol

9) Kc=18.75

10) n(NO2)=6 mol

11) V=13.5 L

16) Kc=0.0715, Kp=3.2

Chapter 8. Redox reactions

1) +6, -2, +4, -0.5

2) +7, -1, +7, +5

3) +4, +7, +3, +7

4) -2, -3, -2, +3

5) -1, +3, +3, +5, +6, -1

6) 1, 4, 1, 2

7) a=4, b=8, c=6; a=2, b=3, c=3

8) Zn(NO3)2, NO, S, NaCl

10) MnO2- reducing agent

11) PtF6 – oxidizing agent

13) 6H+ + 4SO32- + 2MnO4- → 5SO42- + 2Mn2+ + 3H2O

2MnO4- + 5NO2- + 6H+ → 2Mn2+ + 5NO3- + 3H2O

Cr2O72- + 2I- + 14H+ → 2Cr3+ + 7H2O + I2

Cr2O72- + 3NO2- + 8H+ → 2Cr3+ + 4H2O + 3NO3-

14) 3ClO- + 2CrO2 + 2OH- → 3Cl- + 2CrO42- + H2O

8MnO4- + I- + 8OH- → 8MnO42- + IO4- + 4H2O

2MnO2 + 3NO3- + 2OH- → 2MnO4- + 3NO2- + H2O

I- + Cl2 + 6OH- → IO3- + 2Cl- + 3H2O

15) 2,6,1,6,3

3,8,3,2,4

1,4,1,2,2

10, 3,2,5,2,3,1

6,7,1,3,1,7,4

16) 4,10,4,1,3

1,3,1,1,3,1

3,6,5,1,3

1,3,1,3,3

Chapter 9. Analytical methods

1) Mr=117

2) Mr=179, Mr=252, Mr=202

3) Ar(Ne)=20,117

4) Ar(Cl)=35.5

10) C_2H_6O ($C_2H_5OC_2H_5$)

Chapter 10. Halogens

11)

$H_2 + Br_2 \rightarrow 2HBr$

$HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$

12) +1, +1, +3, +7, +5

13) $2NaCl + 2H_2SO_4 + MnO_2 \rightarrow Cl_2 + MnSO_4 + Na_2SO_4 + 2H_2O$

$Cl_2 + 2KI \rightarrow 2KCl + I_2$

14) 469 kJ

15) 8.1 g

16) KCl•NaCl

18) KI, $AgNO_3$

19) $NaClO_3$

20) AgBr, 57.45 g of Ag

21) 6,8,3,6,2,4

1,4,1,1,2

2,1,1,1,1

22) 0.0366 M

3) Q=616 kJ

4) SR=-284.84 J/mol K

5) 8.93%

6) 0.753 M

7) 1.718 M

8) Cl is oxidized and reduced

9) with starch solution

14)

- \- H_2SO_4, electrolysis, KBr, H_2O, H_2O_2, KOH
- \- Na_2CO_3, electrolysis, NaOH, decomposition

- \- KI, HNO_3, KOH, decomposition, electrolysis, NaOH
- \- F_2, H_2O, NaOH

Chapter 11. Alkaline Earth metals

3) $1s^2 2s^2 2p^6 3s^2$

4) $MgSO_4 \times 7H_2O$

5) Mg

6) Radium

7) +2

- –MgO, Mg_3N_2
- \- $CaSiO_3$
- \- $Ca(ClO)_2$, $CaCl_2$, H_2O
- \- CaO, NO_2, O_2

16)

$2Be + 3H_2O \rightarrow BeO + Be(OH)_2 + 2H_2$

$Mg + O_2 \rightarrow MgO$

$Mg + N_2 \rightarrow Mg_3N_2$

$CaH_2 + H_2O \rightarrow Ca(OH)_2 + H_2$

18)

$Be + 2NaOH(conc) + 2H_2O \rightarrow Na_2[Be(OH)_4] + H_2$

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

19) Ba

20) Ca,Ba, Sr, Cu, Fe

21) m(CaH_2)=23.1 g

22) m(BaO)=143 g

23) m(Ca)=42.16 g

24) $Be + 2NaOH + 2H_2O \rightarrow Na_2[Be(OH)_4] + H_2$

m(Be)=1.8 g

25) 0.48 L of N_2O

26) 11.5 L of hydrogen

27)

$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$

$Na_2BeO_2 + 4HNO_3 \rightarrow Be(NO_3)_2 + 2NaNO_3 + 2H_2O$

$Be(NO_3)_2 + 2NaOH(dil) \rightarrow Be(OH)_2 + 2NaNO_3$

$Be(OH)_2 + 2NaOH \rightarrow Na_2[Be(OH)_4]$

$Na_2[Be(OH)_4] + 4HCl \rightarrow BeCl_2 + 2NaCl + 4H_2O$

$3Ca + 2P \rightarrow Ca_3P_2$

$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$

$Ca(OH)_2 \rightarrow CaO + H_2O$

$CaO + CO_2 \rightarrow CaCO_3$

$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

$Ca(HCO_3)_2 + H_2SO_4 \rightarrow CaSO_2 + 2H_2O + 2CO_2$

28)

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

$Ca(OH)_2 \rightarrow CaO + H_2O$

$CaO + 2HCl \rightarrow CaCl_2 + H_2O$

$CaCl_2 + 2KOH \rightarrow Ca(OH)_2 + 2KCl$

$2Ca(OH)_2 + 2Cl_2 \rightarrow Ca(ClO)_2 + CaCl_2 + 2H_2O$

$Ca(ClO)_2 \rightarrow CaCl_2 + O_2$

28)

$BaH_2 + 2H_2O \rightarrow Ba(OH)_2 + 2H_2$

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$

$BaCl_2 + K_2CO_3 \rightarrow BaCO_3 + 2KCl$

$BaCO_3 + H_2SO_4 \rightarrow BaSO_4 + H_2O + CO_2$

29) Be, Ra, Be, Mg, Be, Ca, Mg

30) CM = 0.0025, $[OH^-]=0.005$ M

31) 60 g of solute

32) N = 2×1024

33) 64.9%

34) $CaSO_4$

35) limit reagent is Mg

36) w = 93.3%

37) Cl < Mg < K < Ba

38) Ba

39) CM=0.082 M

40) ΔHr=-690.6 kJ/mol

42) 33% Mg, 67% Ca

43) 60% Cu

44) 4 g of CaCO3

45) 23% of Mg

Chapter 12. Organic Chemistry

1) C4H10, C3H6

Alkanes

1) 2-methyl-4-ethyl-hexane,

3-methyl-4-ethyl-heptane,

2,3,3,6-tetramethyl-heptane,

2-methyl-4-isopropyl-heptane

3) 2,3-dimethylhexane,

2,2-dimethylhexane,

3-methylpentane,

2-methyl-5-ethylheptane

6) butane

8) propane,

$C_3H_6Cl_2$,

propane,

CO_2 and H_2O,

butane and butane

9) Mr=30 g/mol, V(O_2)=15.68 L

10) pentane, 143.36 L of oxygen

11) C_4H_{10}

Empirical and molecular formulas

1) C_4H_{10}

2) C_3H_8

3) C_3H_8O

4) CH_2O

5) $C_2H_2O_4$

Chapter 13. Unsaturated hydrocarbons

1) 3-methylbutene-2

Hexane-1

Hexane-2

6) $C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$

$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$

C2H4 + 3O2 → 2CO2 + 2H2O

2C3H6 + 9O2 → 6CO2 + 6H2O

13) C3H4 + H2 → C3H6

C3H7OH → C3H6 + H2O

14)

- → C2H4
- → CH3CH2CH2CH3
- → CH2=CH-CH3
- → CH3-CH=CH2
- → ZnBr2 + CH3CH2CH2CH2CH2CH3
- → CH2=CH-CH3

15)

C3H8 → C3H6 + H2

C3H7OH → C3H6 + H2O

CH3-CH2-CH2-Br + KOH(alcohol) → CH3-CH=CH2 + KBr + H2O

CH3-CH2-CH2-I + KOH(alcohol) → CH3-CH=CH2 + KI + H2O

16) CH3-C(Cl)(CH3)-CH2-CH2-CH3

18) C5H10 + H2O → C5H11OH

C5H10 + Br2 → C5H10Br2

C5H10 + Cl2 → C5H10Cl2

20)

CH3-C(CH3)=CH-CH3 + HBr → CH3-C(Br)(CH3)-CH2-CH3

CH3-C(CH3)=CH-CH3 + H2 → CH3-CH(CH3)-CH2-CH3

22) n CH2=CH2 → (-CH2-CH2-)n

n CH2=CH-CH3 → (-CH2-CH(CH3)-)n

25) C5H12 + 2Cl2 → C5H10Cl2 + 2HCl

C5H10Cl2 + 2KOH (alcohol) → C5H8 + 2KCl + 2H2O

Chapter 14. Haloalkanes

3) 2-chlorobutane

5) Mr = 154 (CCl4)

6) m(CCl4)=92.4 g (N=1.806×1024)

m(CHBr3)=151.8 g (N=1.806×1024)

m(CH2CHCl)=37.5 g (N=2.167×1024)

7) CHCl3

8) C5H11Br

- → CH3CH2CH2CH2CH2CH3 + 2NaBr
- → CH3CH3 + MgBr2
- → CH3CH=CHCH3

10) 2,3-dimethylbutane

11) 3,4-dimethylhexane

12) methyl bromide, 2-bromobutane

13) 2,3,4-trimethylpentane

14) Mr=30

15) m(Cl2)=196.7 g

16) m(CH3Br)=54.15 g

17) η = 86%

Chapter 15. Alcohols

1) 32, 46, 60, 88

2) 19.2 g, 2.1672×1024

55.2 g, 5.0568×1024

27.6 g, 3.2508×1024

3) 46 g, 32 g

4) C3H8O

5) C5H12O

6) C3H8O3

7) C3H8O

8) CH4O

9) 17.92 L

10) Mr=46

11) C2H6O

12) ethanol, propanol, isobutanol

14) 57.5%

15) 83.87%

19) C3H7OH + Na → C3H7ONa + H2

$C_3H_7OH + CH_3COOH \rightarrow CH_3COOC_3H_7 + H_2O$

$C_3H_7OH + HBr \rightarrow C_3H_7Br + H_2O$

$C_3H_7OH + C_2H_5OH \rightarrow C_2H_5OC_3H_7 + H_2O$

20)

- → $C_2H_5OK + H_2$
- → $CO_2 + H_2O$
- → $CH_3CHO + Cu + H_2O$
- → $C_2H_5OC_2H_5 + H_2O$

21) 8%

22) 3.45%

23)

- → 4-bromohexanol-4
- → 2,2-dimethylbutanol-3
- → 5-methylhexanol-2
- → pentanol-3

24) - C_2H_4

- $CH_3-CH=CH-CH_3$

- $CH_2=CH-C(CH_3)_2-OH$

- $CH_3-CH=CH_2$

28) $V(O_2)=2.24$ L

29) $V(O_2)=8.96$ L

30) $V(O_2)=45.36$ L

31) $C_5H_{11}OH$

32) C4H9OH

33) butanone-2 (CH3COCH2CH3)

34) butanol-2, butanone-2

35) m(CH3COCH3)=8.7 g

- A – H2SO4, ot;

B – HCl;

C – KOH (alcohol);

D – oxidation.

- A – C2H5Br,

B – C4H10,

C – C4H9Br;

D - C4H9OH;

E - C4H9ONa;

F – butyl aldehyde.

- A – 2-chloropropane;

B – 2,3-dimethylbutane;

C - 2,3-dimethyl-2-bromobutane;

D - 2,3-dimethyl-2,3-dibromobutane;

E - 2,3-dimethylbutandiene-1,4.

- A – 2-methylbutene-3;

B - 2-methylbutanol-3;

C - 2-methylbutylate sodium;

D – 2,3-dimethylpropyl-ethyl-ether.

- A – C_2H_5OH;

B – C_2H_5Cl;

C – C_4H_{10};

D – C_4H_9Br;

E – C_4H_8;

F – $C_4H_9OSO_3H$

37) $\chi(C_5H_9OH)=12.5\%$

38) $\omega(C_2H_5OH)=59\%$

39) $\omega(CH_3OH)=58\%$

40) Adding $CaCO_3$,

Adding aqueous Br_2 solution

41) Borax test

GLOSSARY

A

Alcohol - any of a class of chemical compounds having the general formula ROH, where R represents an alkyl group and – OH a hydroxyl group, as in methyl alcohol, CH3OH, or ethyl alcohol, C2H5OH.

Alkene - olefine, olefinany unsaturated aliphatic hydrocarbon with the general formula CnH2n.

Alpha-particle - a positively charged particle consisting of two protons and two neutrons, emitted in radioactive decay or nuclear fission; the nucleus of a helium atom.

Amphoteric - capable of functioning either as an acid or as a base.

Analytical chemistry - the subdivision of chemistry dealing with the qualitative and quantitative determination of chemical components of substances.

Annihilation - the conversion of rest mass into energy in the form of electromagnetic radiation.

Anode - the positive terminal of an electrolytic cell.

Atom - the individual structure which constitutes the basic unit of any chemical element.

Atomic radius - 1.half the distance between the nuclei of two like atoms that are covalently bonded. 2.the experimentally determined radius of an atom in a covalently bonded compound.

Aufbau principle - a description of the building up of the elements in which the structure of each in the sequence is obtained by simultaneously adding one positive charge (proton) to the nucleus of the atom and one negative charge (electron) to an atomic orbital.

Avogadro's law - the principle that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. Thus, the molar volume of all ideal gases at 0°C and a pressure of 1 atm. is 22.4 liters.

Avogadro's number - the constant, 6.022 × 1023, representing the number of atoms, molecules, or ions in one mole of a substance. Symbol: NA

B

Beta-particle - an electron or positron emitted from an atomic nucleus in a certain type of radioactive decay.

Bioethanol - a biofuel based on alcohol which may be combined with petrol for use in vehicles.

Biogas - any gas fuel derived from the decay of organic matter, as the mixture of methane and carbon dioxide produced by the bacterial decomposition of sewage, manure, garbage, or plant crops.

C

Carbocation - a positively charged ion whose charge resides, at least in part, on a carbon atom or group of carbon atoms.

Catalyst - a substance that causes or accelerates a chemical reaction without itself being affected.

Cathode - the electrode at which reduction takes place in an electrochemical cell, that is, a cell through which electrons are being forced.

Chemical bond - a mutual attraction between two atoms resulting from a redistribution of their outer electrons.

Chemical equilibrium - the condition existing when a chemical reaction and its reverse reaction take place at equal rates.

Chromatography - the separation of mixtures into their constituents by preferential adsorption by a solid, as a column of silica (column chromatography) or a strip of filter paper (paper chromatography) or by a gel.

Combustion – 1.rapid oxidation accompanied by heat and, usually, light. 2.chemical combination attended by production of heat and light. 3.slow oxidation not accompanied by high temperature and light.

Covalent bond - the bond formed by the sharing of a pair of electrons by two atoms.

Crude oil - petroleum as it comes from the ground, before refining.

Crystal lattice - the regular array of points about which the atoms, ions, or molecules composing a crystal are centered.

D

Diamond - a pure or nearly pure, extremely hard form of carbon, naturally crystallized in the isometric system.

Dipole – a polar molecule.

E

Electrochemical cell - a combination of two electrodes arranged so that an overall oxidationreduction reaction produces an electromotive force; includes dry cells, wet cells, standard cells, fuel cells, solid-electrolyte cells, and reserve cells.

Electrode potential - the voltage existing between an electrode and the solution or electrolyte in which it is immersed; usually, electrode potentials are referred to a standard electrode, such as the hydrogen electrode. Also known as electrode voltage.

Electrolysis - the passage of an electric current through an electrolyte with subsequent migration of positively and negatively charged ions to the negative and positive electrodes.

Electron - an elementary particle that is a fundamental constituent of matter, having a negative charge of 1.602 × 10−19 coulombs, a mass of 9.108 × 10−31 kilograms, and spin of ½, and existing independently or as the component outside the nucleus of an atom.

Electronegativity - a measure of the ability of a specified atom to attract electrons in a molecule.

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Electronegativity - a measure of the ability of a specified atom to attract electrons in a molecule.

Electronic configuration - the arrangement of electrons in the orbitals of an atom or molecule.

Elimination reaction - a chemical reaction involving elimination of some portion of a reactant compound, with the production of a second compound.

Empirical formula – a chemical formula that indicates the composition of a compound regarding the relative numbers and kinds of atoms in the simplest ratio.

Energy level - one of a quantized series of states in which matter may exist, each having constant energy and separated from others in the series by finite quantities of energy.

Enthalpy - a quantity associated with a thermodynamic system, expressed as the internal energy of a system plus the product of the pressure and volume of the system, having the property that during an isobaric process, the change in the quantity is equal to the heat transferred during the process. Symbol: H.

Entropy – 1. (on a macroscopic scale) a function of thermodynamic variables, as temperature, pressure, or composition, that is a measure of the energy that is not available for work during a thermodynamic process. A closed system evolves toward a state of maximum entropy. 2. (in statistical mechanics) a measure of the randomness of the microscopic constituents of a thermodynamic system. Symbol: S.

F

Fermentation - a change brought about by a ferment, as yeast enzymes, which convert grape sugar into ethyl alcohol.

Free radical - an atom or a diatomic or polyatomic molecule which possesses one unpaired electron.

Functional group - an atom or group of atoms, acting as a unit, that has replaced a hydrogen atom in a hydrocarbon molecule and whose presence imparts characteristic properties to this molecule; frequently represented as R-. Also known as functionality.

G

Gamma-ray - a photon of penetrating electromagnetic radiation (gamma radiation) emitted from an atomic nucleus.

Gasoline - a volatile, flammable liquid mixture of hydrocarbons, obtained from petroleum, and used as fuel for internal-combustion engines, as a solvent, etc.

Geiger counter - an instrument for detecting ionizing radiations, consisting of a gas-filled tube in which electric-current pulses are produced when the gas is ionized by radiation, and of a device to register these pulses: used chiefly to measure radioactivity.

Gibbs free energy - a thermodynamic quantity that is the difference between the internal energy of a system and the product of its absolute temperature and entropy; the capacity of a system to do work, as in an exothermic chemical reaction.

Graphite - a very common mineral, soft native carbon, occurring in black to dark-gray foliated masses, with metallic luster and greasy feel.

H

Haber process - a process for synthesizing ammonia from gaseous nitrogen and hydrogen under high pressure and temperature in the presence of a catalyst.

Halide - a compound of the type MX, where X is fluorine, chlorine, iodine, bromine, and astatine,and M is another element or organic radical.

Haloalkanes - one of a group of halogen derivatives of organic hydrogen- and carboncontaining compounds; the group includes monohalogen compounds (alkyl or aryl halides) and polyhalogen compounds that contain the same or different halogen atoms.

Halogen - any of the elements of the halogen family, consisting of fluorine, chlorine, bromine, iodine, and astatine.

Heat capacity - the heat required to raise the temperature of a substance one degree.

Hess's law - the law that the evolved or absorbed heat in a chemical reaction is the same whether the reaction takes one step or several steps. Also known as the law of constant heat summation.

Homology - that state, in a series of organic compounds that differ from each other by a CH2 such as the methane series CnH2n+2, in which there is a similarity between the compounds in the series and a graded change of their properties.

Hybridization - the mixing together on the same atom of two or more orbitals that have similar energies, forming a hybrid orbital.

Hydrogen bond - a type of chemical bond in which a hydrogen atom that has a covalent link with one of the electronegative atoms (F, N, O) forms an electrostatic link with another electronegative atom in the same or another molecule.

I

Internal energy - a function of thermodynamic variables, as temperature, that represents the internal state of a system that is due to the energies of the molecular constituents of the system. The change in internal energy during a process is equal to the net heat entering the system minus the net work done by the system. Symbol: U

Ionic bond - the electrostatic bond between two ions formed through the transfer of one or more electrons.

Ionization – a process by which a neutral atom or molecule loses or gains electrons, thereby acquiring a net charge and becoming an ion; occurs as the result of the dissociation of the atoms of a molecule in solution or of a gas in an electric field.

Isomer - a compound displaying isomerism with one or more other compounds.

Isotope - atoms of the same element but with a different number of protons and neutrons (i.e. nucleon number). They have nearly identical chemical properties. For example, the two isotopes of chlorine are chlorine-35 and chlorine-37.

M

Mass spectrometer - a device for identifying the kinds of particles present in a given substance: the particles are ionized and beamed through an electromagnetic field and the manner in which they are deflected is indicative of their mass and, thus, their identity.

Mass spectrum - a spectrum of charged particles, arranged in order of mass or mass-tocharge ratios.

Metallic bond - the type of chemical bond between atoms in a metallic element, formed by the valence electrons moving freely through the metal lattice.

Molarity - the number of moles of solute per liter of solution.

Mole - the basic unit in the International System of Units(SI), representing the amount of a substance expressed in grams containing as many atoms, molecules, or ions as the number of atoms in 12 grams of carbon-12 (which is Avogadro's number, or 6.022 × 1023).

Molecular formula - a chemical formula that indicates the kinds of atoms and the number of each kind in a molecule of a compound.

N

Neutron - an elementary particle having no charge, mass slightly greater than that of a proton, and spin of ½: a constituent of the nuclei of all atoms except those of hydrogen. Symbol: n.

Nucleophile - a species possessing one or more electron-rich sites, such as an unshared pair of electrons, the negative end of a polar bond, or pi electrons. Also known as electron donor.

Nucleophilic substitution - a reaction in which a nucleophile bonds to a carbon atom in a molecule, displacing a leaving group. Also known as nucleophilic displacement.

Nucleus - the positively charged mass within an atom, composed of neutrons and protons, and possessing most of the mass but occupying only a small fraction of the volume of the atom.

Nuclide - an atomic species in which the atoms all have the same atomic number and mass number.

O

Organic chemistry – the study of the structure, preparation, properties, and reactions of carbon compounds.

Oxidation – a chemical reaction in which a compound loses electrons that is in which the positive valence is increased.

Oxidation state - the state of an element or ion in a compound with regard to the electrons gained or lost by the element or ion in the reaction that formed the compound, expressed as a positive or negative number indicating the ionic charge of the element or ion.

Oxidizing agent (oxidizer) – a compound that gives up oxygen easily, removes hydrogen from another compound, or attracts negative electrons; also known as an oxidant.

P

Periodic table - a table illustrating the periodic system, in which the chemical elements, formerly arranged in the order of their atomic weights and now according to their atomic numbers, are shown in related groups.

Periodicity - the character of being periodic; the tendency to recur at regular intervals.

Pesticide - a chemical preparation for destroying plant, fungal, or animal pests.

Petroleum - an oily, thick, flammable, usually dark-colored liquid that is a form of bitumen or a mixture of various hydrocarbons, occurring naturally in various parts of the world and commonly obtained by drilling: used in a natural or refined state as fuel, or separated by distillation into gasoline, naphtha, benzene, kerosene, paraffin, etc.

Photon - a quantum of electromagnetic radiation, usually considered as an elementary particle that is its own antiparticle and that has zero rest mass and charge and a spin of one. Symbol: γ.

Polymer - a compound of high molecular weight derived either by the addition of many smaller molecules, as polyethylene, or by the condensation of many smaller molecules with the elimination of water, alcohol, or the like, as nylon.

Polymerization - the act or process of forming a polymer or polymeric compound.

Positron - an elementary particle having the same mass and spin as an electron but having a positive charge equal in magnitude to that of the electron's negative charge; the antiparticle of the electron.

Proton - a positively charged elementary particle that is a fundamental constituent of all atomic nuclei. Symbol: p.

Q

Quantum number - any number that distinguishes among diff erent members of a family of elementary particles.

R

Radioactive decay - the process in which unstable atomic nuclei spontaneously lose some of their excess energy by disintegrating into more stable nuclei. This is accompanied by the emission of alpha particles, beta particles, or gamma rays.

Radioactivity - a qualitative term used to describe the phenomenon resulting from the spontaneous disintegration of atomic nuclei usually with the emission of penetrating radiation or particles.

Rate of reaction - a measurement based on the mass of reactant consumed in a chemical reaction during a given period of time.

Redox reaction - a chemical reaction between two substances in which one substance is oxidized and the other reduced.

Reducing agent (reducer) – 1. a material that adds hydrogen to an element or compound; 2. a material that adds an electron to an element or compound, that is, decreases the positiveness of its valence.

Reduction – 1. reaction of hydrogen with another substance; 2. chemical reaction in which an element gains an electron (has a decrease in positive valence).

Relative atomic mass - the ratio of the average mass per atom of the naturally occurring form of an element to one-twelft h the mass of an atom of carbon-12. Symbol: A r Abbreviation: r.a.m. Former name: atomic weight.

Rubber - also called India rubber, natural rubber, gum, gum elastic, caoutchouc. a highly elastic solid substance, light cream or dark amber in color, polymerized by the drying and coagulation of the latex or milky juice of rubber trees and plants, especially Hevea and Ficus species.

S

Spectroscopy - the science that deals with the use of the spectroscope and with spectrum analysis.

Standard electrode potential - the reversible or equilibrium potential of an electrode in an environment where reactants and products are at unit activity.

Stereoisomers - compounds whose molecules have the same number and kind of atoms and the same atomic arrangement, but differ in their spatial relationship.

Stoichiometry - the calculation of the quantities of chemical elements or compounds involved in chemical reactions.

Structural formula - a chemical formula showing the linkage of the atoms in a molecule diagrammatically, as H–O–H.

Substitution reaction - replacement of an atom or radical by another one in a chemical compound.

T

Thermodynamics - the science concerned with the relations between heat and mechanical energy or work, and the conversion of one into the other: modern thermodynamics deals with the properties of systems for the description of which temperature is a necessary coordinate.

V

Valence electron - an electron of an atom, located in the outermost shell (valence shell) of the atom, that can be transferred to or shared with another atom.

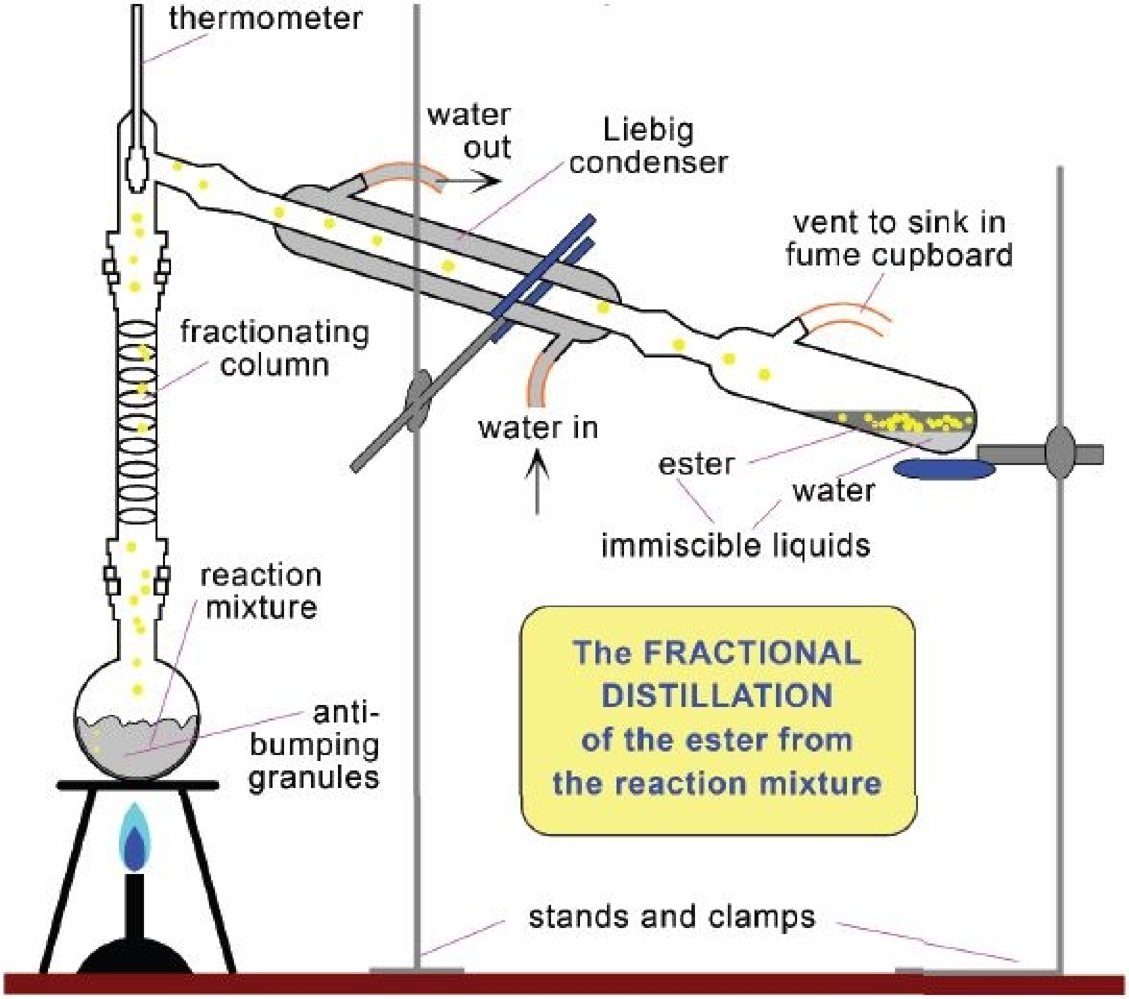
Van der Waals forces - weak, non specific forces between molecules.

Vulcanization - to treat (rubber) with sulfur and heat, thereby imparting strength, greater elasticity, durability, etc.

Y

Yield - the quantity of product formed by the interaction of two or more substances generally expressed as a percentage of the quantity obtained to that theoretically obtainable.

Ester preparation from alcohol and carboxylic acid mixture



APPENDIX A

STANDARD ELECTRODE (REDUCTION) POTENTIALS AT 25ºC

Reaction	E° (V)	Reaction	E° (V)
$Ag^+ + e \rightarrow Ag$	0.7996	$Cu^{2+} + e \rightarrow Cu^+$	0.153
$Al^{3+} + 3e \rightarrow Al$	-1.660	$Cu^{2+} + 2e \rightarrow Cu$	0.3419
$Au^+ + e \rightarrow Au$	1.692	$F_2 + 2e \rightarrow 2F^-$	2.866
$Au^{3+} + 2e \rightarrow Au^+$	1.401	$Fe^{2+} + 2e \rightarrow Fe$	-0.447
$Au^{3+} + 3e \rightarrow Au$	1.498	$Fe^{3+} + 3e \rightarrow Fe$	-0.037
$Ba^{2+} + 2e \rightarrow Ba$	-2.912	$Fe^{3+} + e \rightarrow Fe^{2+}$	-0.771
$Br_2(aq) + 2e \rightarrow 2Br^-$	1.0873	$Fe(OH)_2 + 2e \rightarrow Fe + 2OH^-$	-0.880
$Ca^{2+} + 2e \rightarrow Ca$	-2.868	$2H^+ + 2e \rightarrow H_2$	0.000
$Cd^{2+} + 2e \rightarrow Cd$	-0.403	$2H_2O + 2e \rightarrow H_2 + 2OH^-$	-0.8277
$Cl_2(g) + 2e \rightarrow 2Cl^-$	1.358	$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$	1.776
$Co^{2+} + 2e \rightarrow Co$	-0.280	$Hg^{2+} + 2e \rightarrow Hg$	0.851
$Co^{3+} + e \rightarrow Co^{2+}$	1.920	$2Hg^{2+} + 2e \rightarrow Hg_2^{2+}$	0.920
$Cr^{2+} + 2e \rightarrow Cr$	-0.913	$Hg_2^{2+} + 2e \rightarrow 2Hg$	0.7973
$Cr^{3+} + 3e \rightarrow Cr$	-0.744	$I_2 + 2e \rightarrow 2I^-$	0.5355
$Cr^{3+} + e \rightarrow Cr^{2+}$	-0.407	$K^+ + e \rightarrow K$	-2.931
$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	1.232	$Li^+ + e \rightarrow Li$	-0.304
$CrO_4^{2-} + 4H_2O + 3e \rightarrow Cr(OH)_3 + 5OH^-$	-0.130	$Mg^{2+} + 2e \rightarrow Mg$	-2.372
$Cs^+ + e \rightarrow Cs$	-3.026	$Mn^{2+} + 2e \rightarrow Mn$	-1.185
$Cu^+ + e \rightarrow Cu$	0.521	$Mn^{3+} + e \rightarrow Mn^{2+}$	1.5415
$MnO_2 + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O$	1.224	$Rb^+ + e \rightarrow Rb$	-2.98
$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$	1.507	$S + 2e \rightarrow S^{2-}$	-0.476
$Na^+ + e \rightarrow Na$	-2.710	$Sn^{2+} + 2e \rightarrow Sn$	-0.1375
$Ni^{2+} + 2e \rightarrow Ni$	-0.257	$Sn^{4+} + 2e \rightarrow Sn^{2+}$	0.151
$Pt^{2+} + 2e \rightarrow Pt$	1.18	$Zn^{2+} + 2e \rightarrow Zn$	-0.762

APPENDIX B

STANDARD THERMODYNAMIC VALUES FOR SELECTED SUBSTANCES AT 25°C

Substance	ΔH^0_f (kJ/mol)	ΔG^0_f (kJ/mol)	S^0 (J/mol•K)
Al(s)	0	0	28.3
$AlCl_3$(s)	-704.2	-628.9	110.7
Al_2O_3(s)	-1676	-1582	50.94
Ba(s)	0	0	62.5
$BaCl_2$(s)	-806	-810.9	126
$BaCO_3$(s)	-1219	-1139	112
BaO(s)	-548.1	-520.4	72.07
$BaSO_4$(s)	-1465	-1353	132
B(s)	0	0	5.87
B_2H_6(g)	35	86.6	232
B_2O_3(s)	-1272	-1193	53.8
H_3BO_3(s)	-1094.3	-969	88.83
Br_2(l)	0	0	152.23
Br_2(g)	30.91	3.13	245.38
HBr(g)	-36.3	-53.5	198.59
Ca(s)	0	0	41.6
Ca(g)	192.6	158.9	154.78
CaF_2(s)	-1215	-1162	68.87
$CaCl_2$(s)	-795	-750	114
$CaCO_3$(s)	-1206.9	-1128.8	92.9
CaO(s)	-635.1	-603.5	38.2
$Ca(OH)_2$(s)	-986	-898.6	83.39
$CaSO_4$(s)	-1432.7	-1320	107
C(graphite)	0	0	5.69
C(diamond)	1.896	2.866	2.439
C(g)	715	669.6	158
CO(g)	-110.5	-137.2	197.5
CO_2(g)	-393.5	-394.4	213.7
H_2CO_3(aq)	-698.7	-623.42	191

Substance	**ΔH^0_f (kJ/mol)**	**ΔG^0_f (kJ/mol)**	**S^0 (J/mol•K)**
CH_4(g)	-74.87	-50.81	186.1
C_2H_2(g)	227	209	200.85
C_3H_8(g)	-105	-24.5	269.9
C_6H_6(l)	49	124.5	172.8
C_2H_5OH(l)	-235.1	-168.6	282.6
CH_3COOH(l)	-487	-392	160
$C_6H_{12}O_6$(s)	-1273.3	-910.56	212.1
$C_{12}H_{22}O_{11}$(s)	-2221.7	-1544.3	360.24
CS_2(l)	87.9	63.6	151
Cs(s)	0	0	85.15
Cl_2(g)	0	0	223
Cl(g)	121	105	165.1
HCl(g)	-92.31	-95.30	186.79
HCl(aq)	-167.46	-131.17	55.06
Cr(s)	0	0	23.8
Cu(s)	0	0	33.1
CuO(s)	-157.3	-130	42.63
CuS(s)	-53.1	-53.6	66.5
F_2(g)	0	0	202.7
HF(g)	-273	-275	173.67
H_2(g)	0	0	130.6
I_2(s)	0	0	116.14
I_2(g)	62.44	19.38	260.58
HI(g)	25.9	1.3	206.33
Fe(s)	0	0	27.3
$FeCl_2$(s)	-341.8	-302.3	117.9
$FeCl_3$(s)	-399.5	-334.1	142
FeO(s)	-272	-251.4	60.75
Fe_2O_3(s)	-825.5	-743.6	87.4
Fe_3O_4(s)	-1121	-1018	145.3

Substance	ΔH^0_f (kJ/mol)	ΔG^0_f (kJ/mol)	S^0 (J/mol•K)
Pb(s)	0	0	64.79
PbO(s)	-218	-198	68.7
Li(s)	0	0	29.1
LiF(s)	-616.9	-588.7	35.66
LiCl(s)	-408	-384	59.3
Mg(s)	0	0	32.69
Mg(g)	150	115	148.55
MgO(s)	-601.2	-569	26.9
$MgCO_3$(s)	-1112	-1028	65.86
Hg(l)	0	0	76.03
HgO(s)	-90.79	-58.5	70.27
N_2(g)	0	0	191.5
N_2O(g)	82.05	104.2	219.7
NO(g)	90.29	86.60	210.65
NO_2(g)	33.2	51	239.9
NH_3(g)	-45.9	-16	193
HNO_3(l)	-173.23	-79.91	155.6
O_2(g)	0	0	205
O_3(g)	143	163	238.82
H_2O(l)	-285.8	-237.2	69.94
H_2O(g)	-241.8	-228.6	188.72
H_2O_2(l)	-187.8	-120.4	110
P_4(s) white	0	0	41.1
P(s) red	-17.6	-12.1	22.8
P_4O_{10}(s)	-2984	-2698	229
H_3PO_4(aq)	-1277	-1019	228
K(s)	0	0	64.67
KCl(s)	-436.7	-409.2	82.59
KBr(s)	-394	-380	95.94
KI(s)	-328	-323	106.39
KOH(s)	-424.8	-379.1	78.87

Substance	ΔH^0_f (kJ/mol)	ΔG^0_f (kJ/mol)	S^0 (J/mol·K)
Si(s)	0	0	18
SiF_4(g)	-1614.9	-1572.7	282.4
SiO_2(s)	-910.9	-856.5	41.5
Ag(s)	0	0	47.2
AgF(s)	-203	-185	84
AgCl(s)	-127.03	-109.72	96.11
AgBr(s)	-99.51	-95.94	107.1
AgI(s)	-62.38	-66.32	114
$AgNO_3$(s)	-45.06	19.1	128.2
Na(s)	0	0	51.45
Na(g)	107.76	77.3	153.61
NaCl(s)	-411.1	-384	72.12
NaBr(s)	-361	-349	86.82
NaOH(s)	-425.6	-379.53	64.45
Na_2CO_3(s)	-1130.8	-1048.1	139
$NaHCO_3$(s)	-947.7	-851.9	102
NaI(s)	-288	-285	98.5
S(rhombic)	0	0	31.9
S(monoclinic)	0.3	0.096	32.6
S_8(g)	101	49.1	430.2
H_2S(g)	-20.2	-33	205.6
SO_2(g)	-296.8	-300.2	248.1
SO_3(g)	-396	-371	256.7
H_2SO_4(l)	-814	-690	156.9
H_2SO_4(aq)	-907.5	-742	17
Sn(s) white	0	0	51.5
SnO_2(s)	-580.7	-519.7	52.3
Zn(s)	0	0	41.6
ZnO(s)	-348	-318.2	43.9

VALENCIES OF COMMON IONS

Name	Valency	Symbol	Name	Valency	Symbol
Ammonium	1	NH_4^+	Acetate	1	CH_3COO^-
Copper(I) or cuprous	1	Cu^+	Bicarbonate	1	HCO_3^-
Cesium	1	Cs^+	Hydrogensulfate	1	HSO_4^-
Potassium	1	K^+	Hydrogensulfite	1	HSO_3^-
Silver	1	Ag^+	Bromide	1	Br^-
Sodium	1	Na^+	Chloride	1	Cl^-
Lithium	1	Li^+	Chlorate	1	ClO_3^-
Hydrogen	1	H^+	Cyanide	1	CN^-
Barium	2	Ba^{2+}	Fluoride	1	F^-
Calcium	2	Ca^{2+}	Hydride	1	H^-
Cobalt(II)	2	Co^{2+}	Hydroxide	1	OH^-
Copper(I) or cupric	2	Cu^{2+}	Iodide	1	I^-
Iron(II) or ferrous	2	Fe^{2+}	Nitrate	1	NO_3^-
Lead (II)	2	Pb^{2+}	Nitrite	1	NO_2^-
Magnesium	2	Mg^{2+}	Permanganate	1	MnO_4^-
Mercury(II) or mercuric	2	Hg^{2+}	Carbonate	2	CO_3^{2-}
Nickel	2	Ni^{2+}	Chromate	2	CrO_4^{2-}
Strontium	2	Sr^{2+}	Dichromate	2	$Cr_2O_7^{2-}$
Tin(II) or stannous	2	Sn^{2+}	Oxide	2	O^{2-}
Zinc	2	Zn^{2+}	Sulfide	2	S^{2-}
Aluminium	3	Al^{3+}	Sulfite	2	SO_3^{2-}
Chromium	3	Cr^{3+}	Sulfate	2	SO_4^{2-}
Iron(III) or ferric	3	Fe^{3+}	Nitride	3	N^{3-}
Tin(IV) or stannic	4	Sn^{4+}	Phosphate	3	PO_4^{3-}

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CHEMISTRY

Grade 10

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