

Introduction to bioinorganic chemistry. Hydrogen and water.

Lecture 1

Main topics of the lecture:

- The biosphere;
- Classification of biogenic elements;
- Positions of biogenic elements in the periodic table;
- Chemical properties of hydrogen and its compounds;
- Chemical properties of water.

The structure of our planet according to geology

–*lithosphere;*

–*hydrosphere;*

–*atmosphere.*

The borders of biosphere

Biosphere is the part of Earth in which living organisms can survive and breed. Areas on the boarder of litho-, atmo- and hydrosphere are especially enriched by living organisms.

The borders of biosphere:

- The lower part of biosphere (troposphere) – **15-20 km** (lower than the ozone layer). The part of atmosphere near the ground or ocean is enriched by living species.
- The whole hydrosphere – down to the bottom of ocean (**10 km**).
- The upper part of lithosphere – down to the depth of **3.5 – 7.5 km**. But just soil is enriched by living species.

Well-known survivors

- *Deinococcus radiodurans*

37% of these bacteria survive under the influence of radiation equal to 15000 Gr (5 Gr is enough to kill any human)

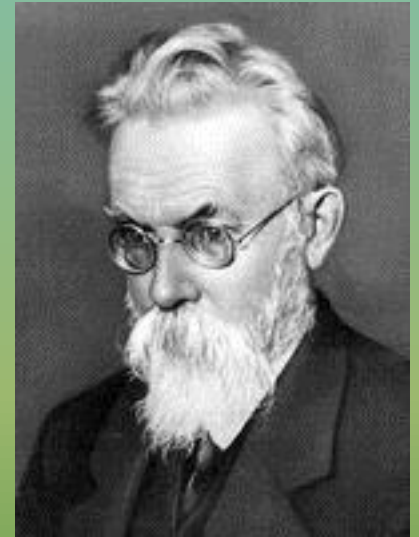
- *Sulfolobus acidocaldarius*

prefers high temperature and strongly acidic medium:

t° 75 – 80 °C, pH 2-3.

From biosphere to noosphere

- Vladimir Ivanovich Vernadsky
(1863 – 1945)
- «One of the factors which will lead a humankind to the creation of noosphere is the development of the common worldwide system for the information exchange».



The content of Earth crust and living organisms

	O	Si	Al	Fe	Ca	Mg	Na	K	H	P	C	Cl	S	N
Lithosphere	49	26	7,5	4,2	3,2	2,4	2,4	2,4	1,0	0,7	0,35	0,20	0,10	0,04
Biosphere	<u>65</u>	< 0,01	< 0,001	< 0,1	1,4	< 0,1	0,26	0,27	<u>10</u>	<u>0,9</u>	<u>18,5</u>	<u>0,25</u>	<u>0,21</u>	<u>2,65</u>

The wide sense of the term “Biogenic elements”

Biogenic elements are those chemical elements which are **always present** in living organisms and perform certain **biological functions.**

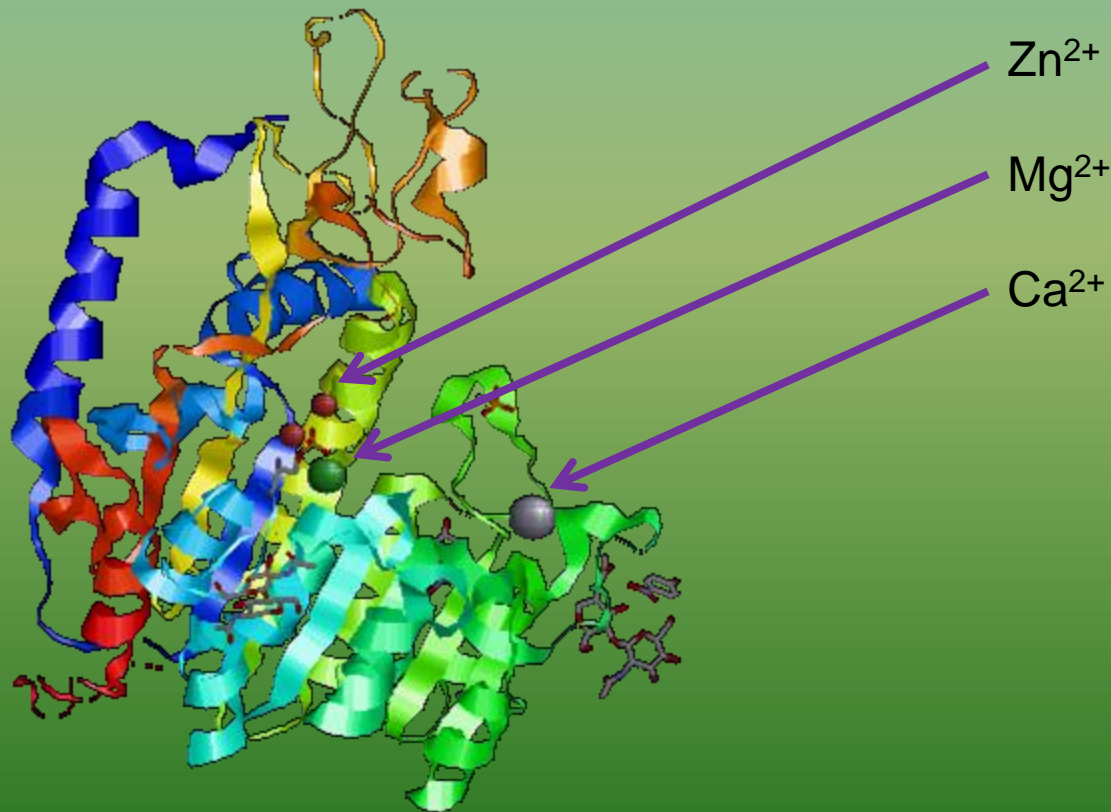
More concrete definition of the term “Biogenic elements”

- From 92 elements known to exist in Nature, 81 elements are found in organisms of animals.
- There are four criteria that must be satisfied for a biogenic element:
 - **It must be present permanently** in the organisms of the same species **in the same quantities**;
 - The concentration of an element is different in different tissues and organs: **some tissues are enriched by a given element**;
 - Synthetic ration without a given element causes specific symptoms of insufficiency by the way of **biochemical changes in tissues**;
 - These **symptoms disappear after the return of a given element into the ration.**

Bioelementomics

- Bioelementomics is the science on the roles of chemical elements in metabolism.
- Elementomics is another name of the same science of bioelementomics.
- The largest part of bioelementomics is called “metallomics” that is about the roles of metals in metabolism.
- Metallome is the set of metalloenzymes and metalloproteins, as well as other metal containing biomolecules.

3D structure of human placental alkaline phosphatase



Classifications of biogenic elements

- Classification according to the **functional role**:

- **Organogenes** – the elements that build up organic substances: C, H, O, N, P, S. About 97-98% of a body mass are due to these six elements.

An average content of proteins (by mass):

C – 51-55%;

H – 6.5-7.0%;

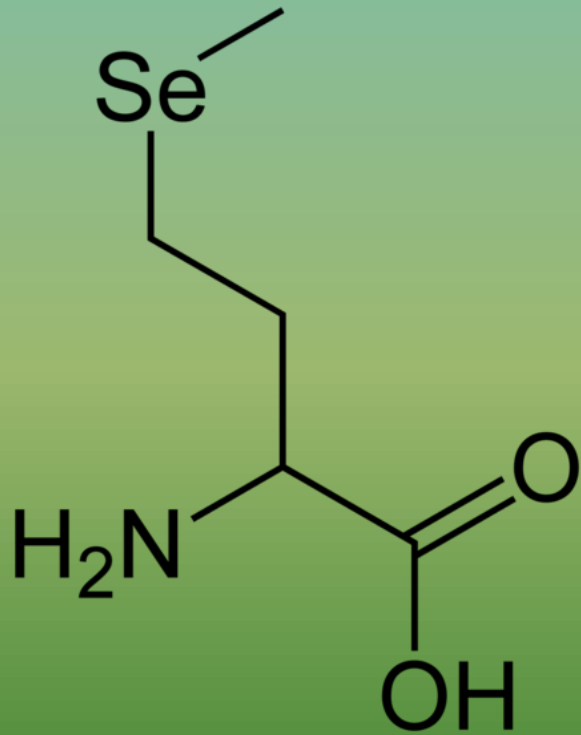
O – 22-24%;

S – 0.3-2.5%;

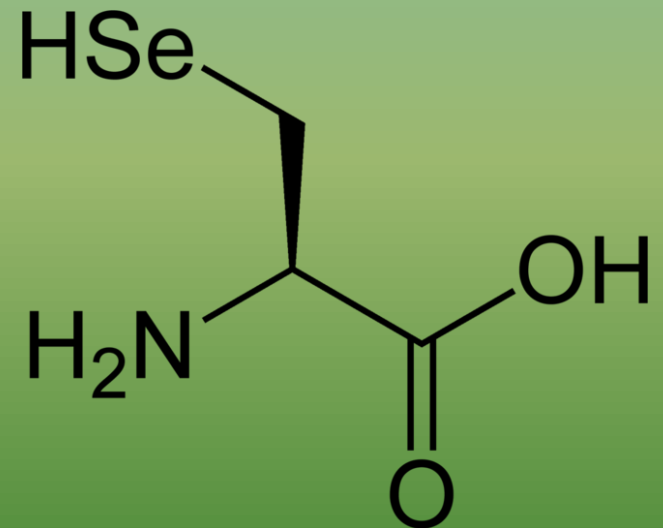
N – 15-18%;

P – 0.5%.

Selenium – is it a seventh organogene?



selenomethionine



selenocysteine

- **Elements of electrolytic background**: Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- . Ions Na^+ , K^+ , Mg^{2+} and Ca^{2+} make up about 99% of the mass of all metals in the organism.
- **Microelements** are chemical elements building up active centers of enzymes, stabilizing the structure of proteins, hormones and other biologically active molecules. Examples: Zn^{2+} - carbanhydrase, carboxypeptidase; Fe^{3+} - catalase, peroxidase; Mo^{6+} - aldehyde oxidase; Co^{2+} - ribonucleotide reductase.

Classification of biogenic elements according to their content

- **Macroelements** are biogenic elements with a content higher than 0.01% of the body weight. They are: six organogenes (C, H, O, N, P, S), ions of the electrolytic background (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^-) and *iron*. Macroelements make up 99.99% of the body weight.
- **Microelements** are biogenic elements with a content from 10^{-3} until 10^{-5} % of the body weight. Among them there are: Zn, Mn, Mo, Cu, I, F, Br and others.
- **Ultramicroelements** are biogenic elements with a content less than 10^{-5} % of the body weight. Among them there are: Al, Cr, Se and others.

- Microelements become dangerous at increased concentrations when they demonstrate their toxic effects.
- Interestingly, a toxic element arsenic is a known (since 19th century) biostimulator at low concentrations.
- There are no toxic elements, but there are toxic concentrations.
- Paracelsus: «Everything is poisonous. But the low dosage may hide that poison».

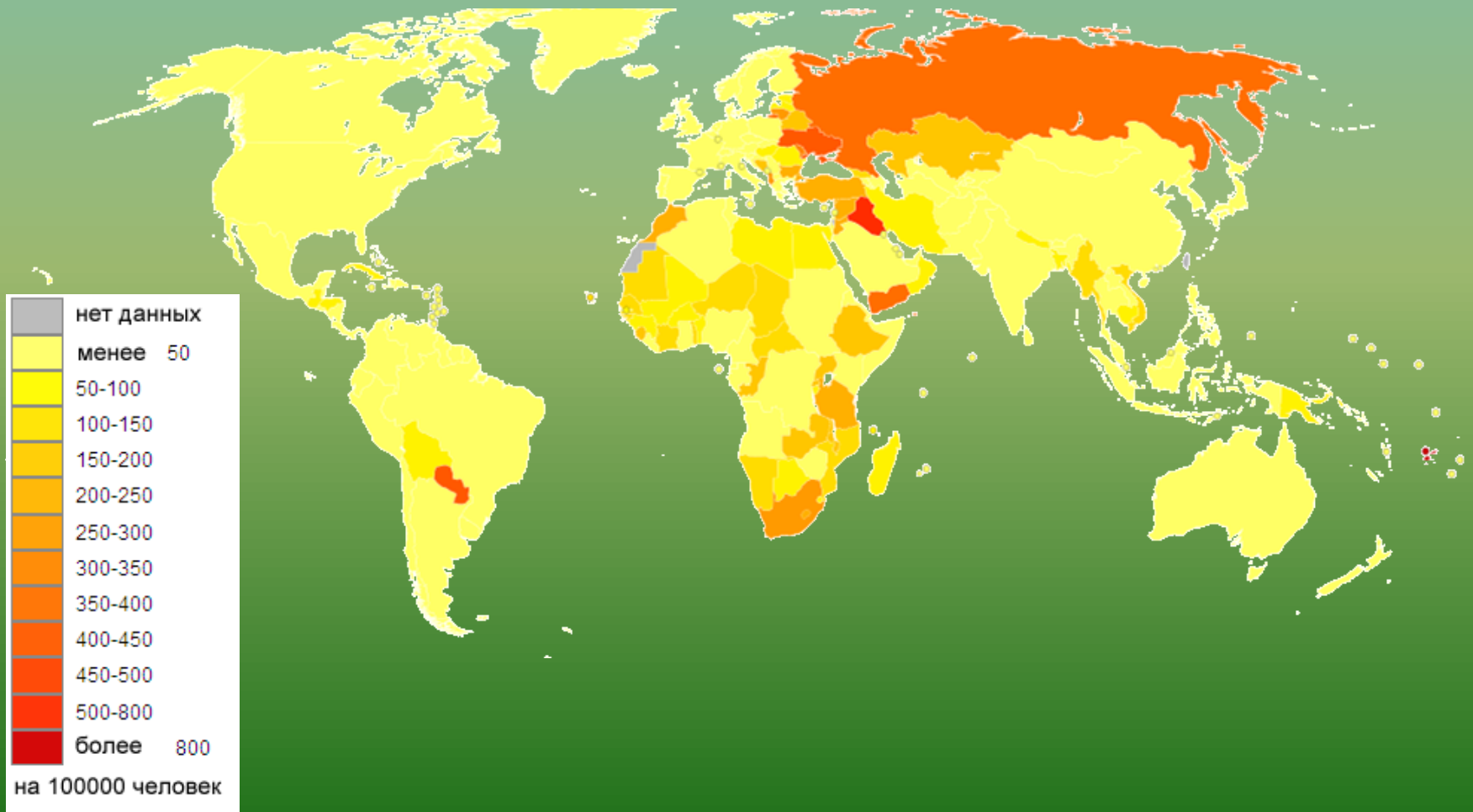
Biogeochemical provinces.

Endemic diseases

- Biogeochemical provinces are the territories with the excess or the lack of certain chemical element(s). Organisms living in these territories and eating the products grown in them suffer from specific reactions called endemic diseases.
- Endemic disease is a disease caused by the excess or the lack of certain biogenic or toxic elements because of their unusual concentrations in the ration. Endemic disease is spread only in the certain territory.

- Insufficiency of microelements:
 - Fe - anemia
 - Co - anemia (megaloblastic)
 - F - caries
 - I - hypothyroid
 - Se - sudden death syndrome
 - Cr - symptoms of diabetes
- Increased content of microelements:
 - Fe - syderosis
 - Mo - gout
 - Cu - Wilson disease

Iodine insufficiency frequency in 2002



Biogeochemical provinces with iodine insufficiency



The mass percentage of certain chemical elements in the human body

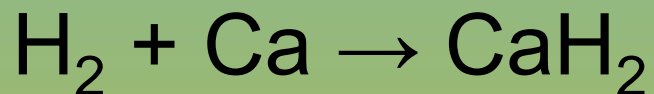
Cu	$1 \cdot 10^{-4}$	Zn	$1 \cdot 10^{-3}$	Ca	1,9
Ag	$5 \cdot 10^{-6}$	Cd	$1 \cdot 10^{-4}$	Sr	$1 \cdot 10^{-3}$
Au	$1 \cdot 10^{-7}$	Hg	$1 \cdot 10^{-7}$	Ba	$1 \cdot 10^{-5}$

Hydrogen

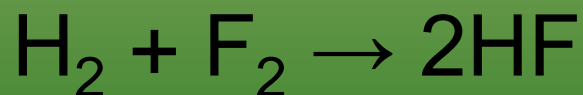
- Hydrogen is the most widespread element in the Universe. 92% of atoms are thought to be hydrogen atoms. About 8% of atoms are helium atoms. What is left for all other elements? Just about 0.1%.
- The mass fraction of hydrogen in the Earth crust is near 1%. It holds the 10th place among all elements.
- The mole fraction of hydrogen in the Earth crust is about 17%. It holds the 2nd place among all elements (after oxygen).

Chemical properties of hydrogen

- At normal temperature hydrogen reacts only with active metals producing hydrides



- and with just one nonmetal – with fluorine – producing hydrogen fluoride



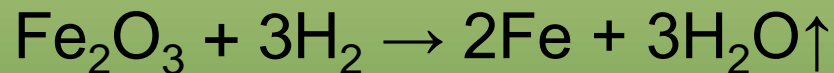
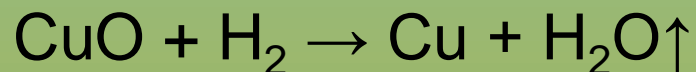
Chemical properties of hydrogen

- $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$
- $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$
- $\text{S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$
- $\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$

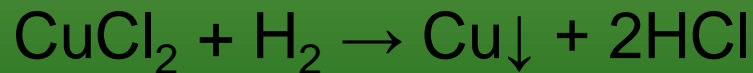
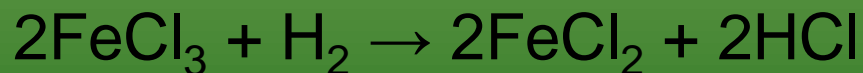
Reaction between oxygen and hydrogen is accompanied by a burst.

Chemical properties of hydrogen

As a reducer hydrogen is used for the production of pure metals from their oxides. This way is good for the reduction of metals standing to the right from zinc (including zinc itself) in the electrochemical series of metals.



Hydrogen can reduce iron (III) chloride and copper (II) chloride from their water solutions.



Hydrides of alkali and alkaline-earth metals

- $\text{KH} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{H}_2\uparrow$
- $\text{CaH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{H}_2\uparrow$
- $\text{CaH}_2 + \text{O}_2 \rightarrow \text{Ca(OH)}_2$

The ways to produce hydrogen in the laboratory

- $\text{CaH}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{H}_2\uparrow$
- $2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \rightarrow 2\text{Na[Al(OH)}_4] + 3\text{H}_2\uparrow$
- $\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2\uparrow$
- $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2\uparrow$

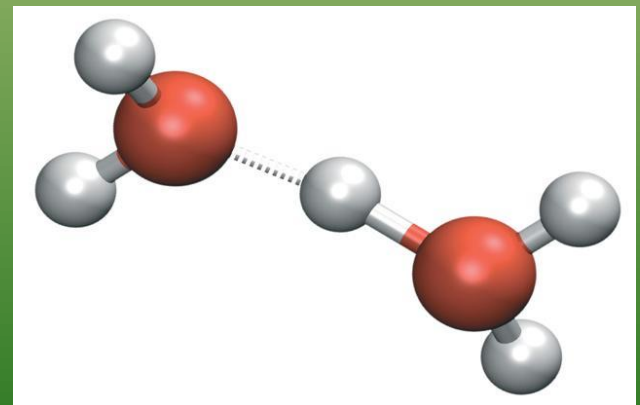
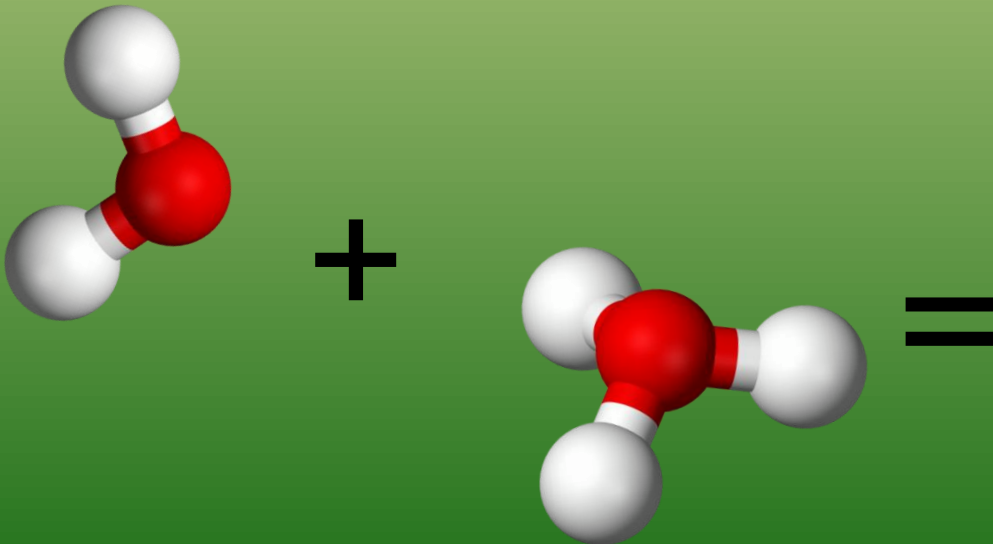
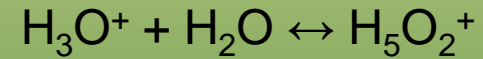
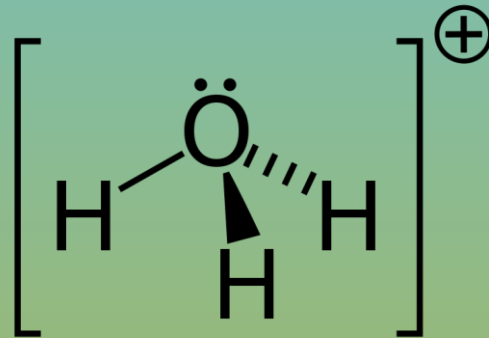
The apparatus of Kipp

With the help of the Kipp apparatus one can collect gases produced in a chemical reaction between solid and liquid phases.

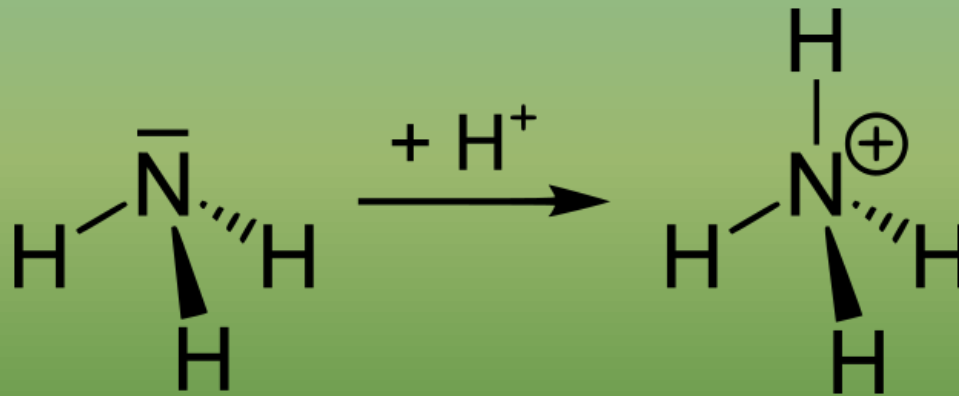
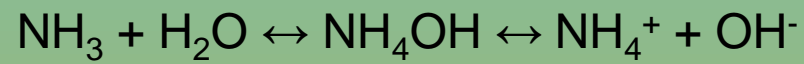


Production of hydrogen

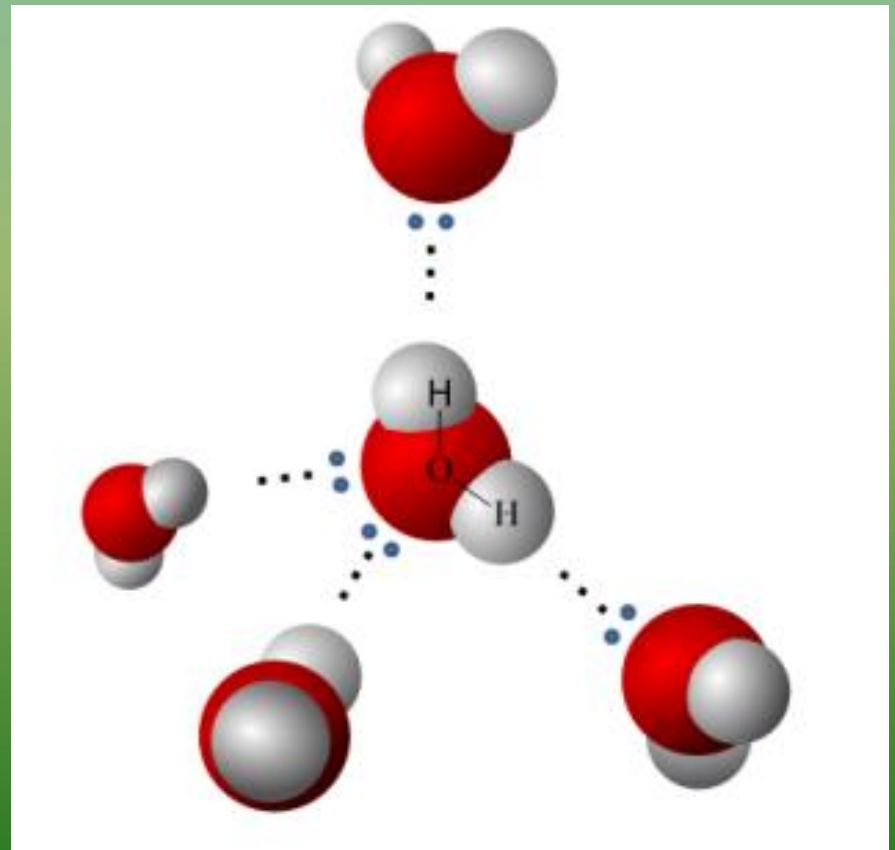
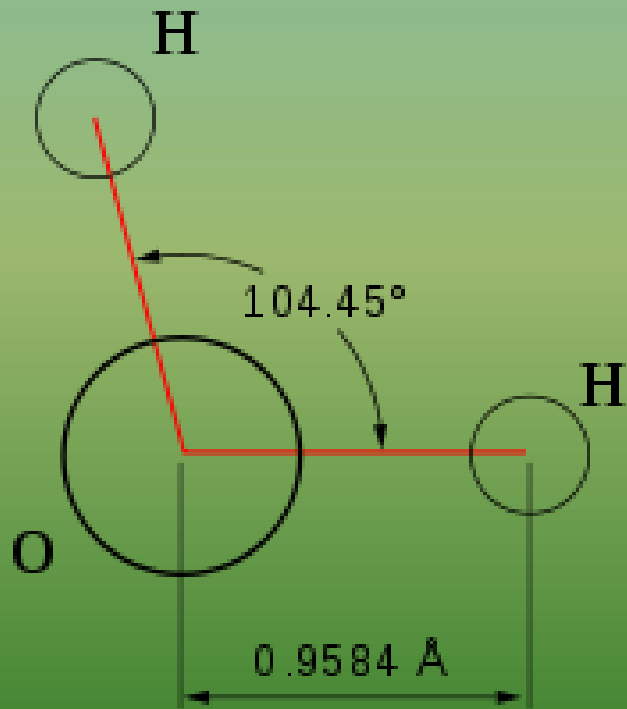
Hydronium ion



Ammonium ion



The structure of a water molecule



Physical properties of water

- High temperature of boiling;
- High temperature of melting;
- High enthalpy of evaporation;
- High enthalpy of melting;
- The highest heat capacity;
- High viscosity;
- High surface tension.

Chemical properties of water

- At room temperature water reacts with:
 - active metals (Na, K, Ca, etc.);
 - halogens;
 - basic and acidic oxides;
 - salts;
 - hydrides, carbides, silicides, nitrides, phosphides of active metals.

Hydrolysis of certain binary compounds

- $\text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2\uparrow$
- $\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3\downarrow + 3\text{CH}_4\uparrow$
- $\text{Ca}_2\text{Si} + 4\text{H}_2\text{O} \rightarrow 2\text{Ca(OH)}_2 + \text{SiH}_4\uparrow$
- $\text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg(OH)}_2\downarrow + 2\text{NH}_3\uparrow$
- $\text{Mg}_3\text{P}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg(OH)}_2\downarrow + 2\text{PH}_3\uparrow$

Electrolysis of water

Water hardness

- Water hardness is the group of chemical and physical properties of water that appear because of the high content of calcium and magnesium cations.
- TH – $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$
- PH – CaSO_4 , CaCl_2 , MgSO_4 , MgCl_2

The best way to express the hardness is the sum of Ca^{2+} and Mg^{2+} concentrations (mmol/L)

The methods to decrease the hardness

- Boiling: $\text{Ca}(\text{HCO}_3)_2 = \text{CaCO}_3\downarrow + \text{CO}_2 + \text{H}_2\text{O}$
- The usage of reactants: (Na_2CO_3 , $\text{Ca}(\text{OH})_2$):
 $\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 = 2\text{CaCO}_3\downarrow + 2\text{H}_2\text{O}$
 $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3\downarrow + 2\text{NaCl}$
- Cation exchange
- Reversed osmosis

Biological role of water

- From 55 % to 78 % of the mass of an organism are due to water. The loss of more than 10 % of water may cause death.
- Normally a human organism needs about 3 L of water each day.
- Water is the component of blood and lymph, urine, cerebrospinal fluid, digestive juices, and... intracellular liquid.

Biological role of water

- Water is able to hydrolyze not just inorganic salts, but lipids, proteins and carbohydrates during digestion and catabolism.
- Turgor
- The regulation of body temperature

Natural water

- Underground water;
- Water released during the melting of snow and ice;
- Water of rivers, lakes, seas and oceans

Mineral water «Darida»

- Chemical content of “Darida”, mg/L
- **Na⁺ + K⁺ 990-1400**
- **Ca²⁺ 30-65**
- **Mg²⁺ 10-35**
- **SO₄²⁻ 340-500**
- **Cl⁻ 1250-1700**
- **HCO₃⁻ 180-350**

Mineral water «Minskaya-4», with fluorides

Anions, mg/L

Cl^-	1500-2100
HCO_3^-	180-280
SO_4^{2-}	350-500
F^-	1,0-5,0

Cations, mg/L

$\text{Na}^+ + \text{K}^+$	1100-1700
Ca^{2+}	< 100
Mg^{2+}	< 100

Mineral water «Borjomi»

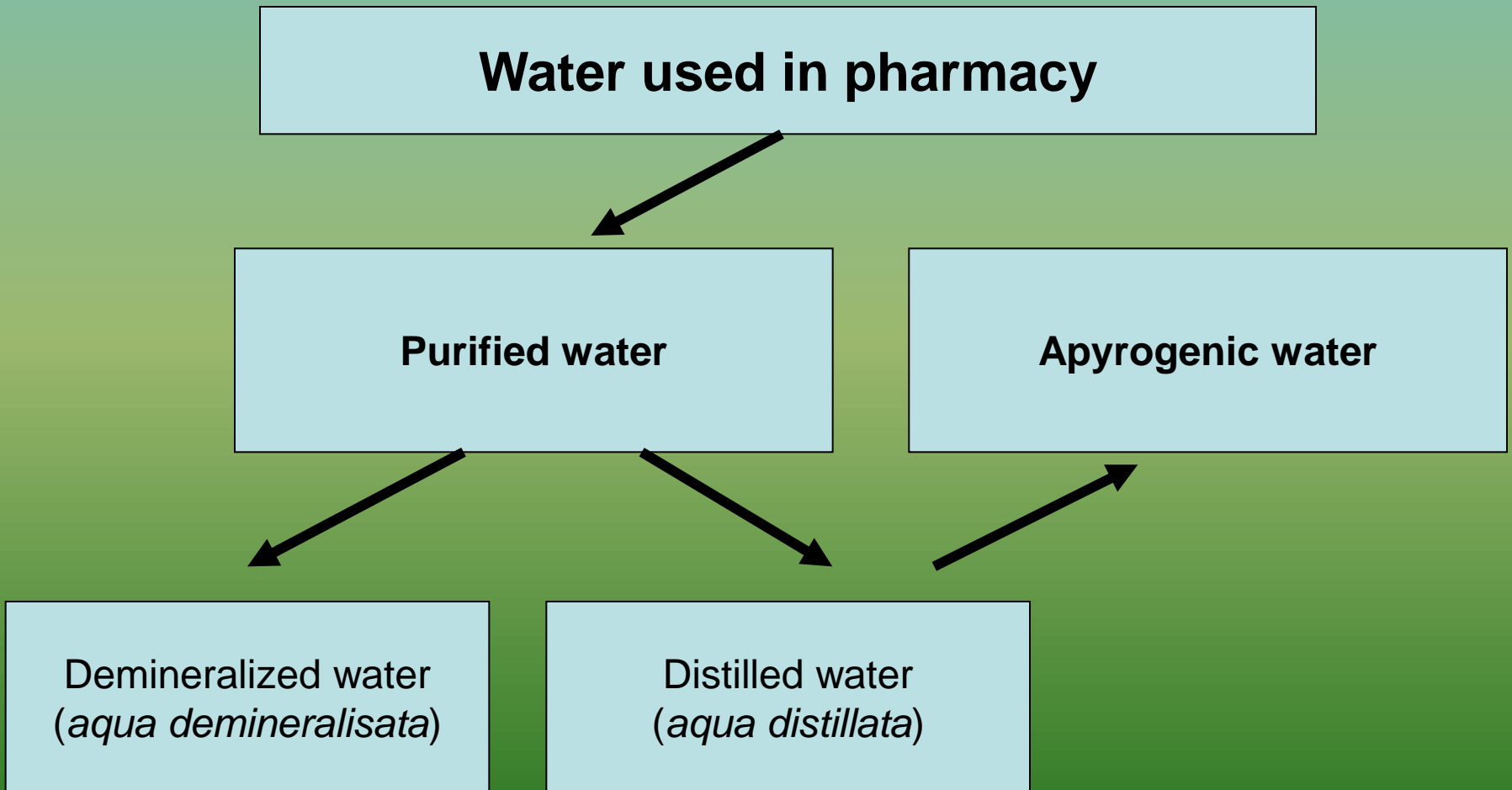
Anions, mg/L

Cl^-	250-500
HCO_3^-	3500-5000
SO_4^{2-}	< 10
F^-	800 mcg / 100 g

Cations, mg/L

$\text{Na}^+ + \text{K}^+$	1000-2000
Ca^{2+}	20 – 150
Mg^{2+}	20 – 150

Purified and apyrogenic water



Apyrogenic water

- That water has no molecules able to cause the temperature rise after the intravenous injection.
- Such water is used to dissolve medicines for intravenous injections.

Thank you for listening!