

Chemical properties
of s-elements
and their compounds
Lecture 2

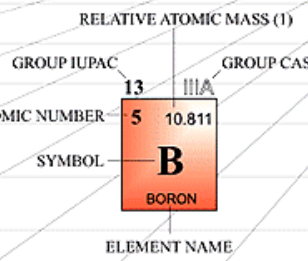
The plan of the lecture

1. Overall characteristic of s^1 and s^2 elements
2. Natural resources of s^1 and s^2 elements
3. Physical and chemical properties of s -elements and their compounds
4. Biological roles, the usage in medicine and pharmacy, test reactions for compounds made from s -elements

PERIODIC TABLE OF THE ELEMENTS

<http://www.ktf-split.hr/periodni/en/>

PERIOD	GROUP	1	2	13	14	15	16	17	18										
		IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA										
1		1 1.0079 H HYDROGEN							2 4.0026 He HELIUM										
2		3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM																
3		11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM																
4		19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5		37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6		55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7		87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uu UNUNNIUM	111 (272) Uu UNUNUNIUM	112 (285) Uu UNUNBIUM		114 (289) Uu UNUNQUADIUM				



Legend:

- Metal (Blue)
- Semimetal (Orange)
- Nonmetal (Green)

Classification:

- 1 Alkali metal
- 2 Alkaline earth metal
- Transition metals (Blue)
- Lanthanide (Pink)
- Actinide (Purple)
- 16 Chalcogens element
- 17 Halogens element
- 18 Noble gas

STANDARD STATE (25 °C; 101 kPa)

- Ne - gas
- Fe - solid
- Ga - liquid
- Tc - synthetic

LANTHANIDE

57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERIUM	71 174.97 Lu LUTETIUM
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ACTINIDE

89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM
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(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements having no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.

However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Properties of s¹-elements

Properties	Li	Na	K	Rb	Cs
Metallic radius, nm	0,152	0,186	0,227	0,248	0,265
Ionic radius , nm	0,068	0,102	0,138	0,149	0,170
The charge density	14,7	9,8	7,2	6,7	5,9
The radius of hydrated ion, nm	0,340	0,276	0,232	0,228	0,228
Enthalpy of hydration, $\Delta H_{\text{hydr}}E^+$, kJ/mol	-500	-390	-305	-280	-246
Ionization energy, eV $I_1, E^0 \rightarrow E^+ + e^-$	5,390	5,138	4,339	4,176	3,893
Electronegativity	0,98	0,93	0,82	0,82	0,79

Li, K, Ba, Ca, Na, Mg, Al, Mn, Zn, Cr, Fe, Co, Sn, Pb, H_2 , Cu, Hg, Ag, Au

$$\begin{aligned} &\Delta H \text{ hydration} < 0 \\ &+ \\ &\Delta H \text{ oxidation} > 0 \\ &+ \\ &\Delta H \text{ atomization} > 0 \end{aligned}$$

Properties of s²-elements

Свойство	Be	Mg	Ca	Sr	Ba	Ra
Metallic radius, nm	0,113	0,160	0,197	0,215	0,221	0,235
Ionic radius , nm	0,034	0,074	0,104	0,120	0,138	0,144
The charge density	58,8	27,0	19,2	16,7	14,5	13,9
The radius of hydrated ion, nm	0,460	0,440	0,420	0,420	0,410	-
Enthalpy of hydration, $\Delta H_{\text{hydr}} E^+$, kJ/mol	9,32	7,65	6,11	5,69	5,21	5,28
Ionization energy, eV $I_1, E^0 \rightarrow E^+ + e^-$	0,98	0,93	0,82	0,82	0,79	

Natural resources of s-elements

Halite - NaCl



Silvinite – $m\text{NaCl} \cdot n\text{KCl}$



Natural resources of s-elements

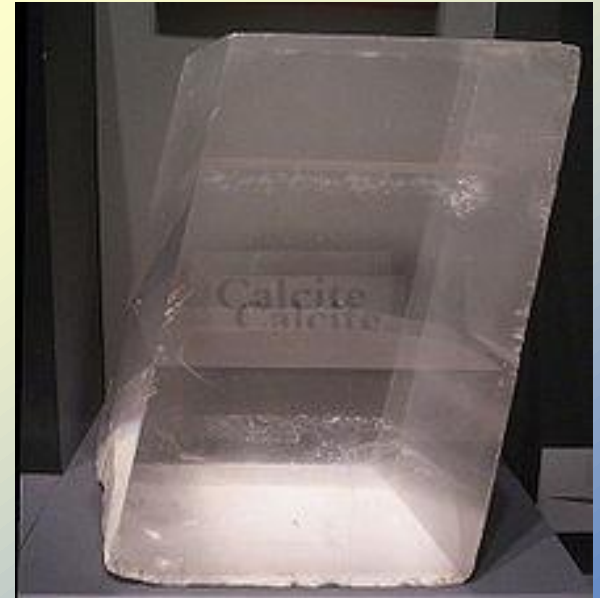
Calcite / chalk / limestone /
marble = «the sunlight stone»
– CaCO_3



Magnesite – MgCO_3



Dolomite – $\text{CaCO}_3 \cdot \text{MgCO}_3$



Physical properties of alkali metals

Chemical properties of s-elements

- The products of their reactions with pure chemical elements: NaH ; Na_2C_2 ; Na_4Si ; Na_3N ; Na_3P ; Na_2O ; Na_2S ; NaF ; NaCl ; NaI
- They can react with water and acids
- Oxides (Na_2O ; K_2O ; CaO) – are purely basic (except BeO)
- Hydroxides (NaOH ; KOH ; $\text{Ca}(\text{OH})_2$) – are strong bases (except $\text{Be}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$)

Superoxides, peroxides and oxides

- $2\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$
- $4\text{Na} + \text{O}_2 \rightarrow 2\text{Na}_2\text{O}$
- $\text{Na}_2\text{O}_2 + 2\text{Na} \rightarrow 2\text{Na}_2\text{O}$
- $2\text{K} + \text{O}_2 \rightarrow \text{K}_2\text{O}_2$
- $\text{K} + \text{O}_2 \rightarrow \text{KO}_2$
- $\text{K}_2\text{O}_2 + 2\text{K} \rightarrow 2\text{K}_2\text{O}$
- $\text{KO}_2 + 3\text{K} \rightarrow 2\text{K}_2\text{O}$
- $\text{Na}_2\text{O}_2 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O}_2$
- $2\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{NaOH} + \text{O}_2\uparrow$

Reaction of an alkali metal and water

- *«Alkali metals react with water at room temperature».*
- Sodium and potassium melt soon after the start of the reaction because of the release of big amount of heat and low temperatures of melting
- Hydrogen produced in the reaction between potassium and water burns (it reacts with oxygen from the air).

Reactions between Li, Na and K with H₂O

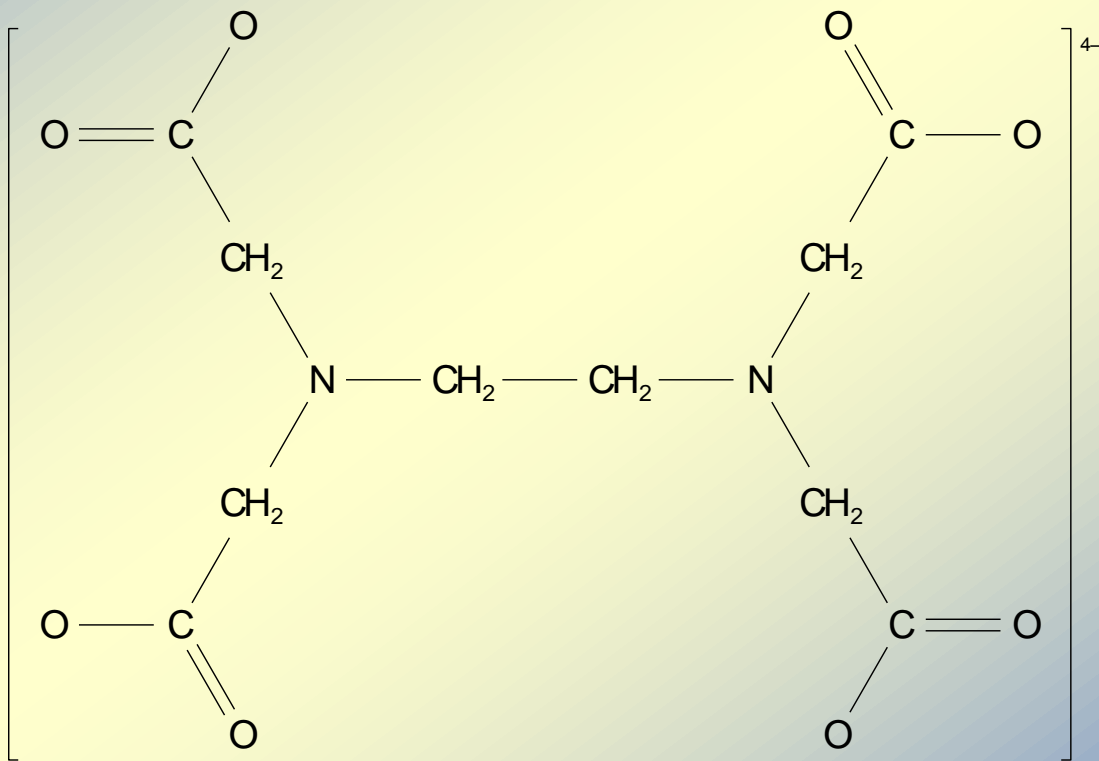
Aquatic complexes and salt hydrates

- In water solutions cations of s-elements exist as aquatic complexes:
- $[\text{Li}(\text{H}_2\text{O})_4]^+$; $[\text{Na}(\text{H}_2\text{O})_6]^+$;
- $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$; $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$; $[\text{Ca}(\text{H}_2\text{O})_6]^{2+}$
- They also can form salt hydrates:
- $\text{CaCl}_2 \cdot 6\text{H}_2\text{O} = [\text{Ca}(\text{H}_2\text{O})_6]\text{Cl}_2$
- $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

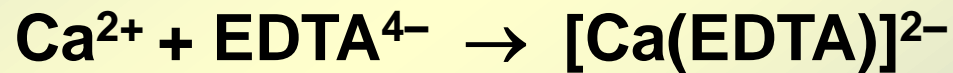
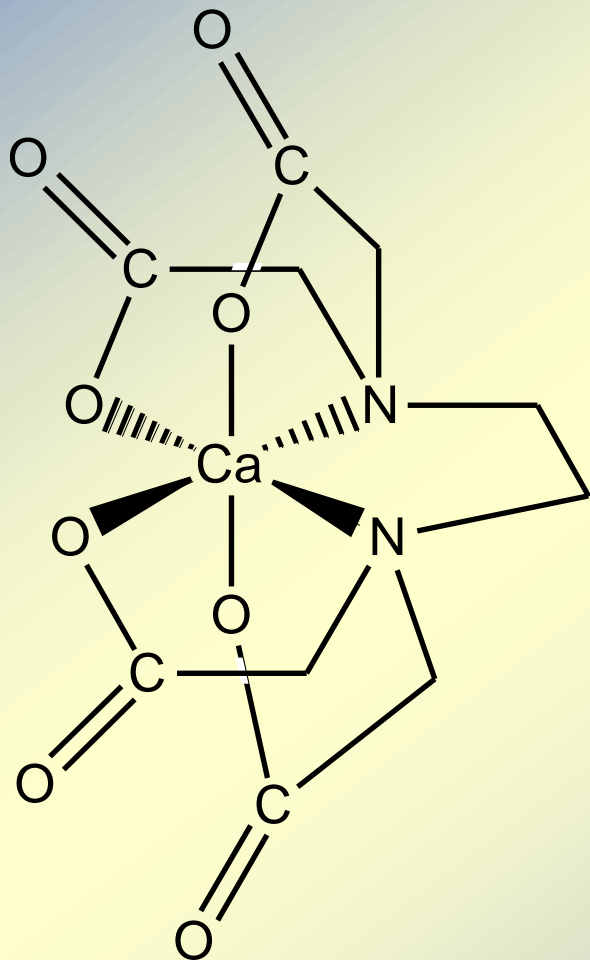
Complex compounds

- Magnesium, calcium, strontium and barium can form stable complexes with polydentate ligands like polyamino polycarbonic acids.

The formula of ethylenediaminetetraacetate ion (EDTA⁴⁻)

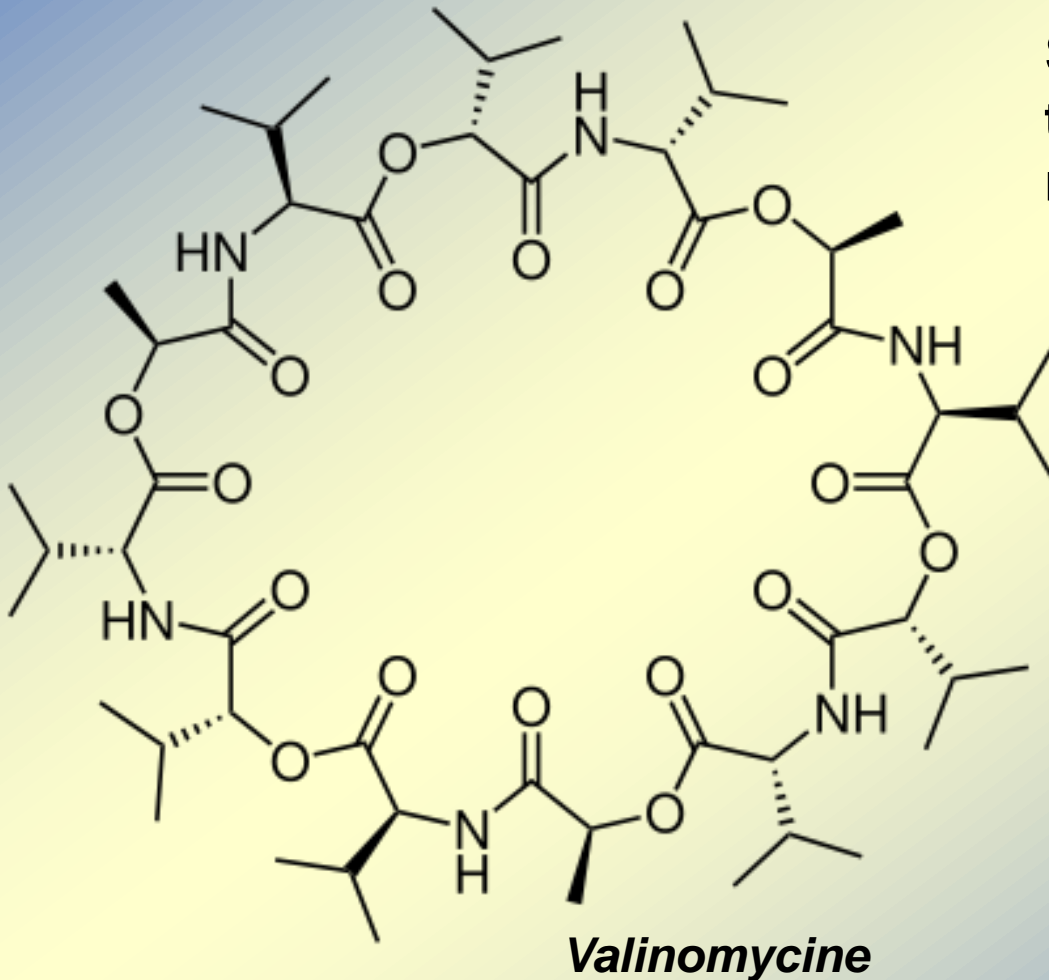


The structure of EDTA complex with Ca^{2+}



Ionophores

Such molecules serve as ion transporters through cell membrane

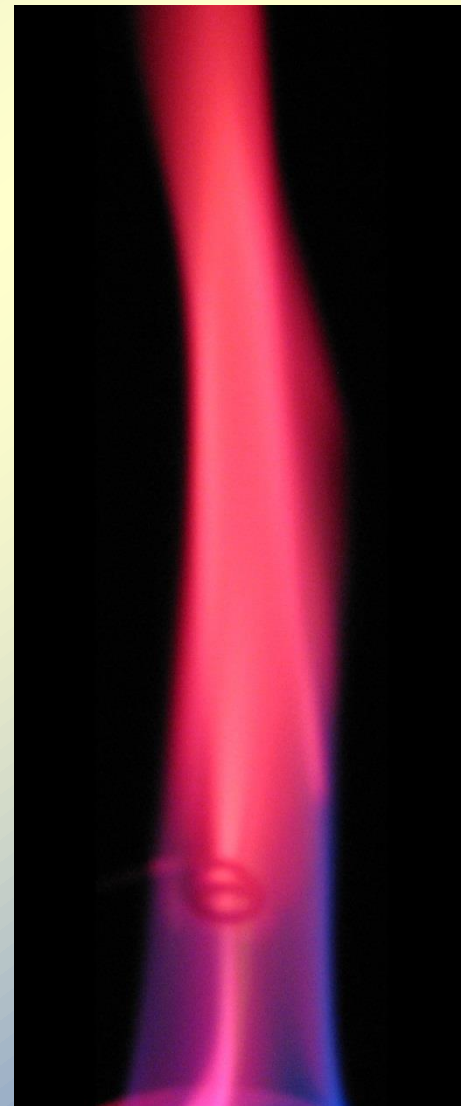
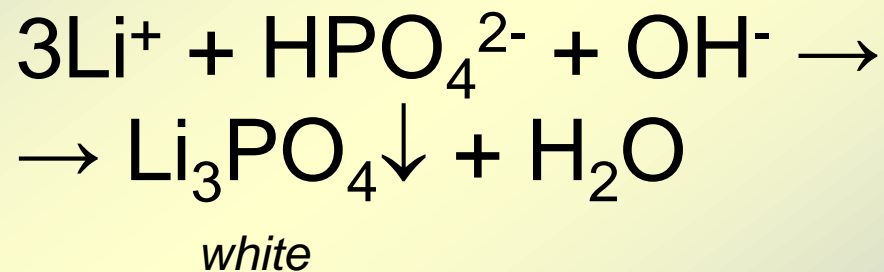


Medicines containing lithium cations

- Li_2CO_3 – antipsychotic drug
- Lithium benzoate is used to treat gout as a part of urodan.

Test reactions for lithium salts

The color of flame becomes carmine-red when you burn a lithium salt



Biological role of sodium

1. Na^+ – is the most abundant cation of intercellular liquid and blood: it is responsible of the most part of their osmotic pressure
 - Increased sodium concentration in blood – (> 145 mmol/L) leads to dehydration of neurons
 - Decreased sodium concentration in blood – (< 135 mmol/L) leads to hyperhydration of neurons
2. Na^+ ions take part in the creation of bioelectric membrane potential

Medicines containing sodium salts

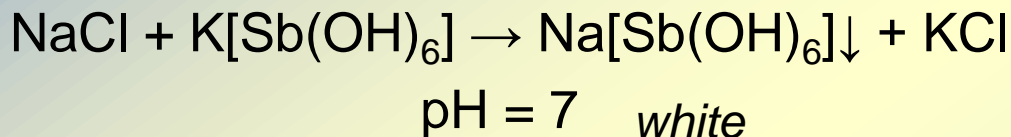
- NaF – to prevent and treat caries
- NaCl – in physiological solution (0.85%) and hypertonic solutions (3, 5 and 10%)
- NaBr – sedative drug
- NaI – to compensate the lack of iodine
- Sodium citrate is used for blood conservation
- $\text{Na}_2\text{S}_2\text{O}_3$ – to treat scabies

Medicines containing sodium cations

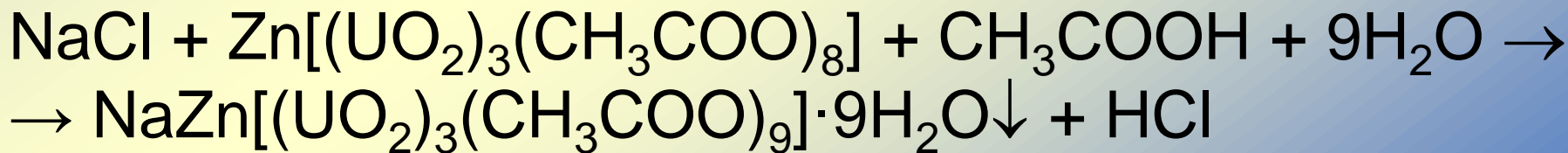
- NaHCO_3 – table soda;
- $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – Glaubert's salt;
- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ – borax

Test reactions for sodium cations

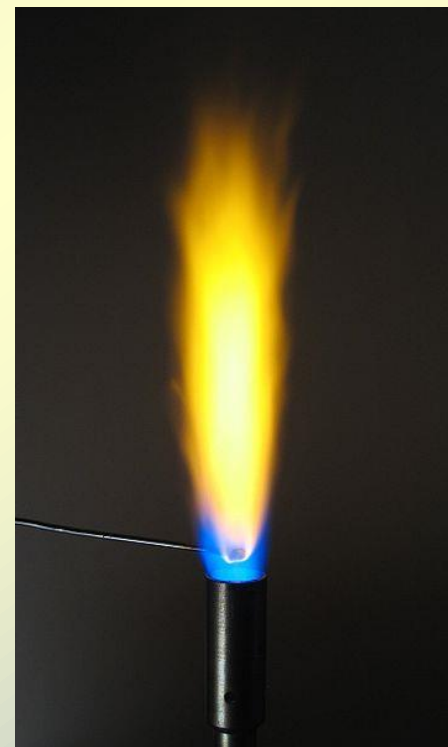
- Na^+ cations turn the color of the flame to yellow



zinc uranylacetate



Yellow-green crystals



Biological role of potassium cations

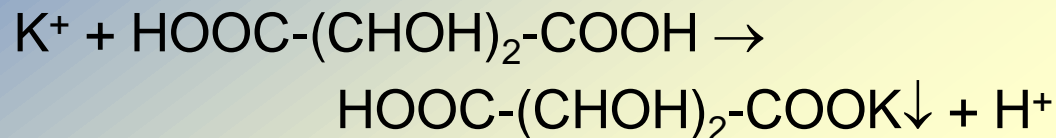
1. K^+ – are the most abundant cations of the intracellular liquid: they play an important role in its osmotic pressure formation
2. K^+ – play important role in the creation of bioelectric membrane potential
3. They are important for glucose transport
4. The decrease of potassium blood level ($< 3 \text{ mmol/L}$) – leads to muscular weakness and increased heart beat rate
5. The increase of potassium blood level ($> 5.5 \text{ mmol/L}$) – leads to the decreased heart beat rate

Medicines containing potassium ions

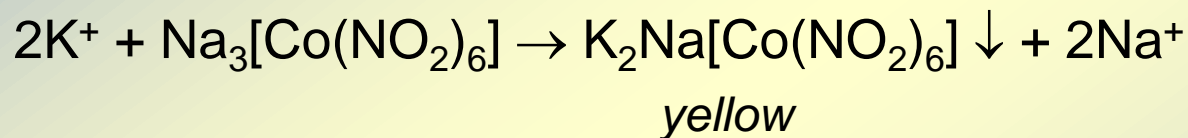
- KCl – to compensate the lack of potassium
- KBr – sedative drug
- KI – to compensate the iodine deficiency
- KMnO_4 – is used as disinfectant
- CH_3COOK – is a diuretic
- Potassium and magnesium asparaginate – are included in polyvitamin and polymineral complexes

Test reactions for potassium salts

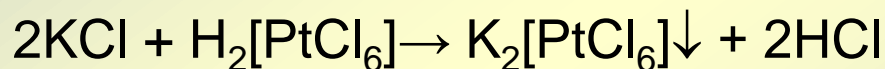
Tartric acid



*Potassium hydrogen tartrate -
white*



yellow



yellow

Potassium salts turn the color
of the flame to violet



Physical and chemical properties of cesium

- Cesium is the most active stable metal.
- Cesium is found mostly in muscles, in the heart, in the liver. Its blood level is below 2.8 mcg/L.
- Cesium is not very toxic, but its biological roles are still to be explored.

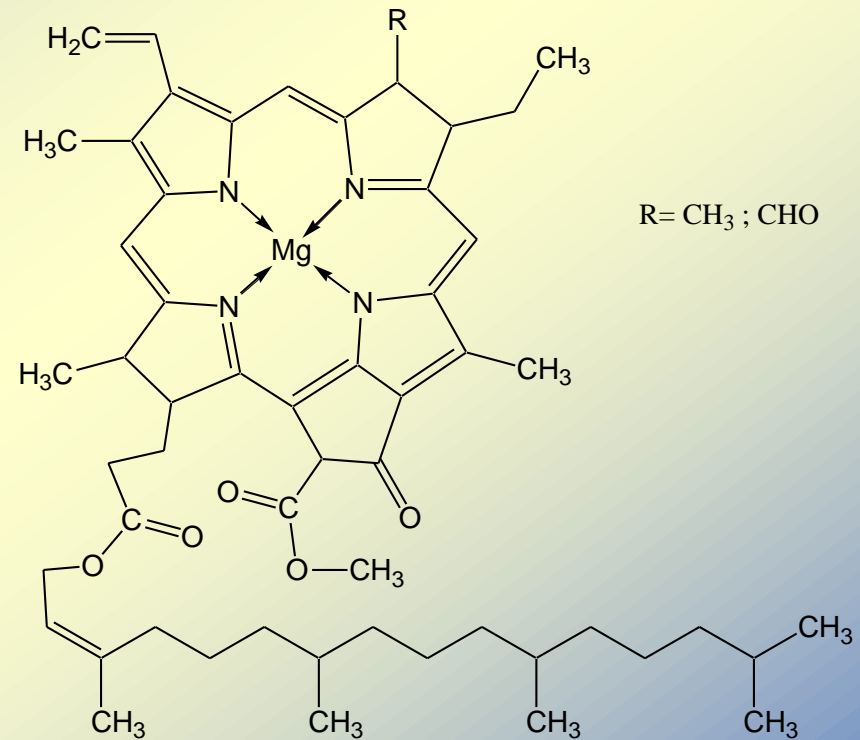
Reaction of cesium and oxygen from the air

Beryllium is toxic

- Beryllium dust and soluble compounds are highly toxic, they demonstrate allergic and cancerogenic effects. Beryllium can replace calcium and magnesium in bones and in active centers of important enzymes. The resulting disease is called berylliosis.

Biological roles of magnesium

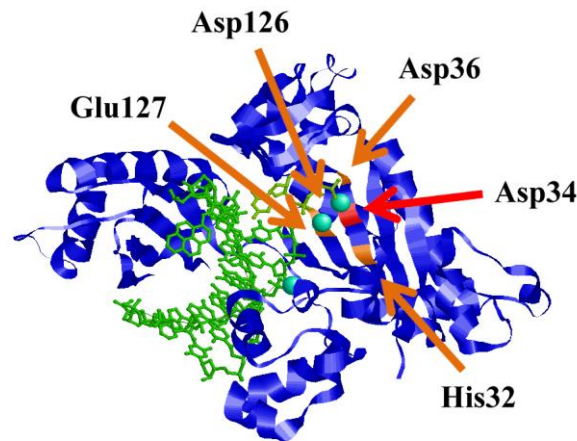
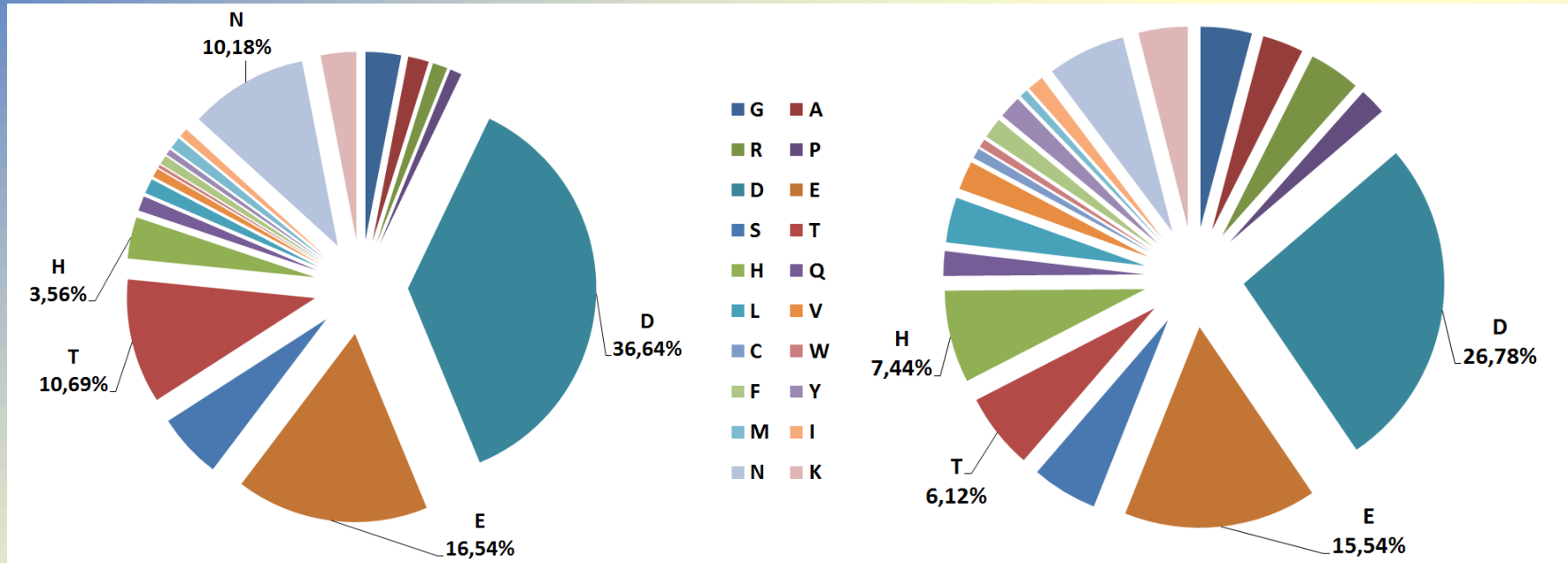
- Mg^{2+} - is found in chlorophyll
- It holds the second place among intracellular cations
- These ions are important co-factors for enzymes involved in replication



Mg²⁺ binding sites in proteins

With another ligand (phosphate)

without other ligands



Interactions of Mg and H₂O

- With cold water magnesium reacts slowly.
- Compact magnesium reacts with hot water and form magnesium oxide (hydrogen is released in this process).
- $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2$
- Highly dispersed magnesium still can form $\text{Mg}(\text{OH})_2$ in the reaction with hot water.
- $\text{Mg} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + \text{H}_2$

Medicines containing magnesium salts

- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ – «English salt»;
- MgSO_4 – 25% water solution – has hypotonic, analgesic and choleric effects;
- MgCO_3 – is an antacid, prevents stomach ulcers;
- $(\text{MgOH})_2\text{CO}_3$ – is also an antacid;
- MgO – is an antacid as well

Medicines containing magnesium salts

- Magnesium citrate – compensates the lack of Mg^{2+}
- Polyvitamin and polymineral complexes usually contain lactate, orotate or asparginate of magnesium.
- Glutamate and ascorbate of magnesium have a hypotonic effect

Test reactions for magnesium salts

- Magnesium compounds burn with a shiny white color of a flame
- $\text{MgSO}_4 + \text{Na}_2\text{HPO}_4 + \text{NH}_3 \rightarrow \text{MgNH}_4\text{PO}_4 \downarrow + \text{Na}_2\text{SO}_4$

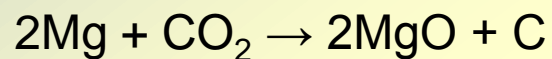
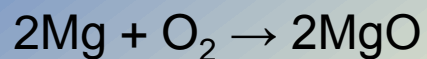
*Orthophosphate of
magnesium and
ammonium*

white,

soluble in CH_3COOH

Magnesium combustion

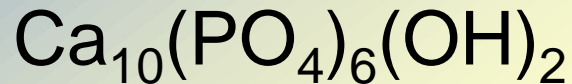
Magnesium can be “burnt” in carbon dioxide



Combustion of calcium

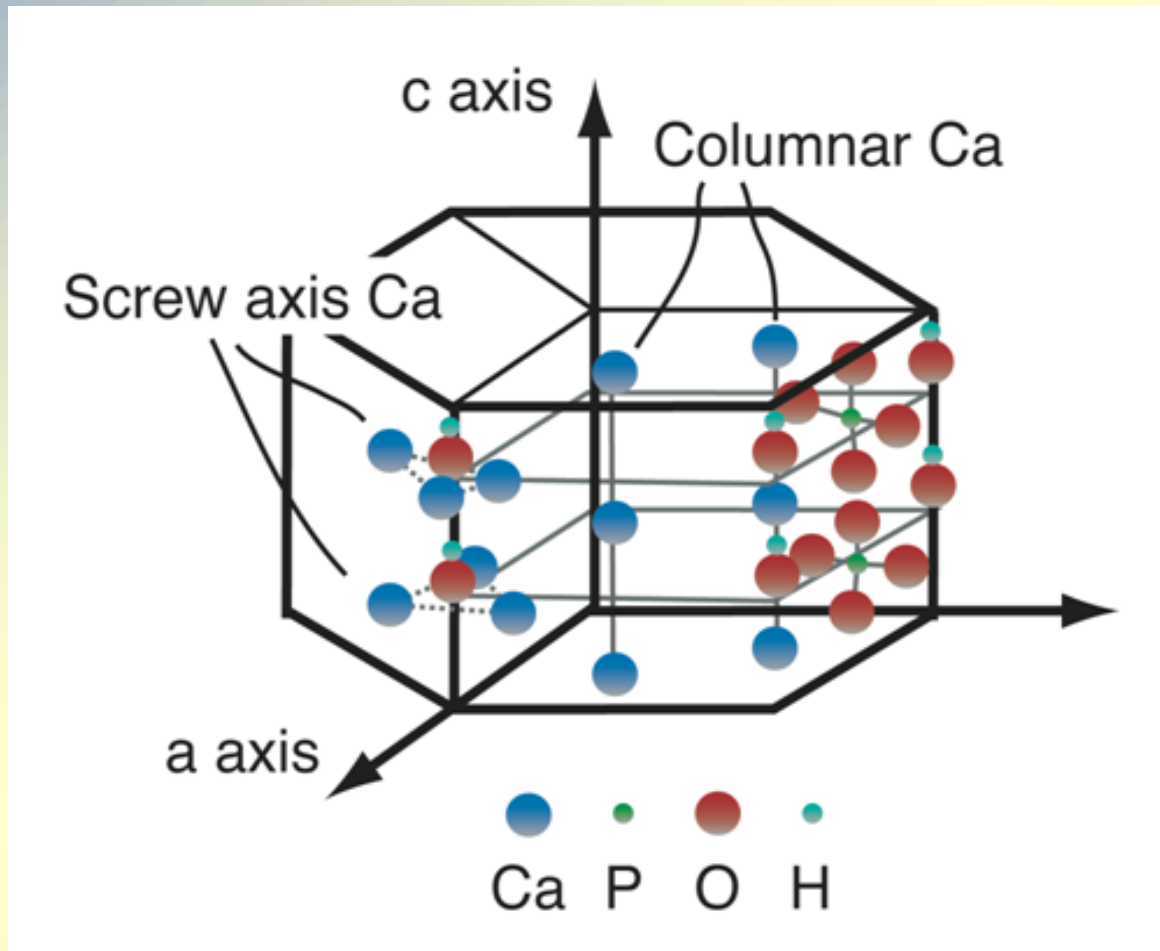
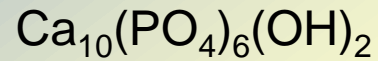
Biological roles of calcium

1. The most part of calcium is concentrated in the bone tissue

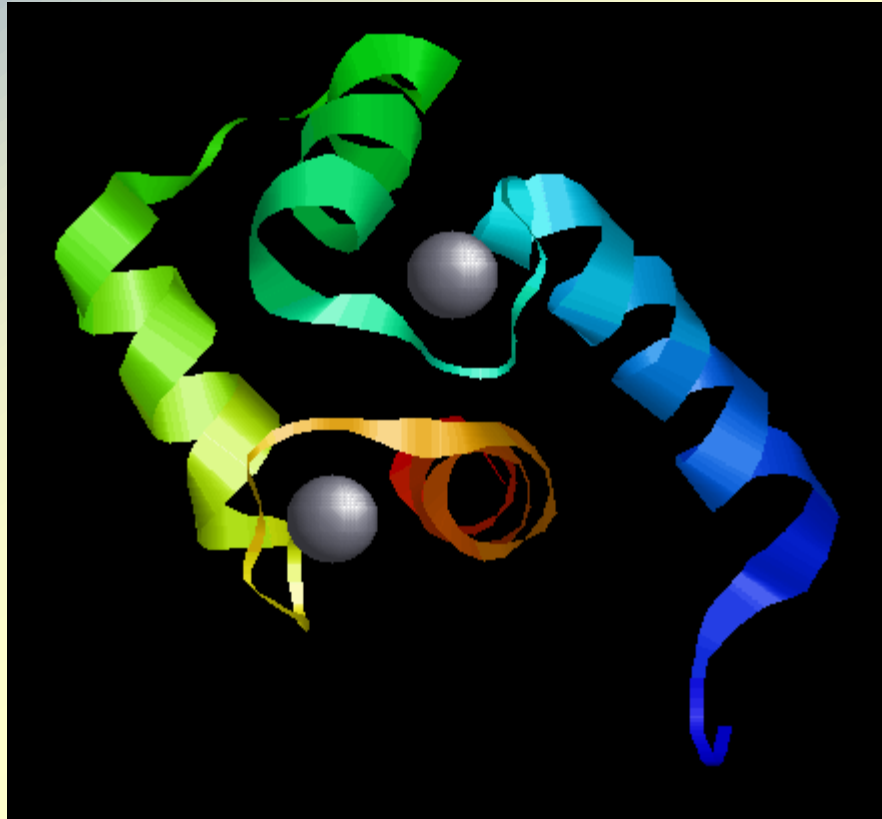


2. Ca^{2+} – has higher concentration outside the cells than inside them
3. These ions are important for muscle contraction
4. Ca^{2+} is a factor needed for the formation of thrombus (clot)
5. Ca^{2+} is an activator of enzymes
6. Ca^{2+} is a secondary messenger

Calcium hydroxyapatite

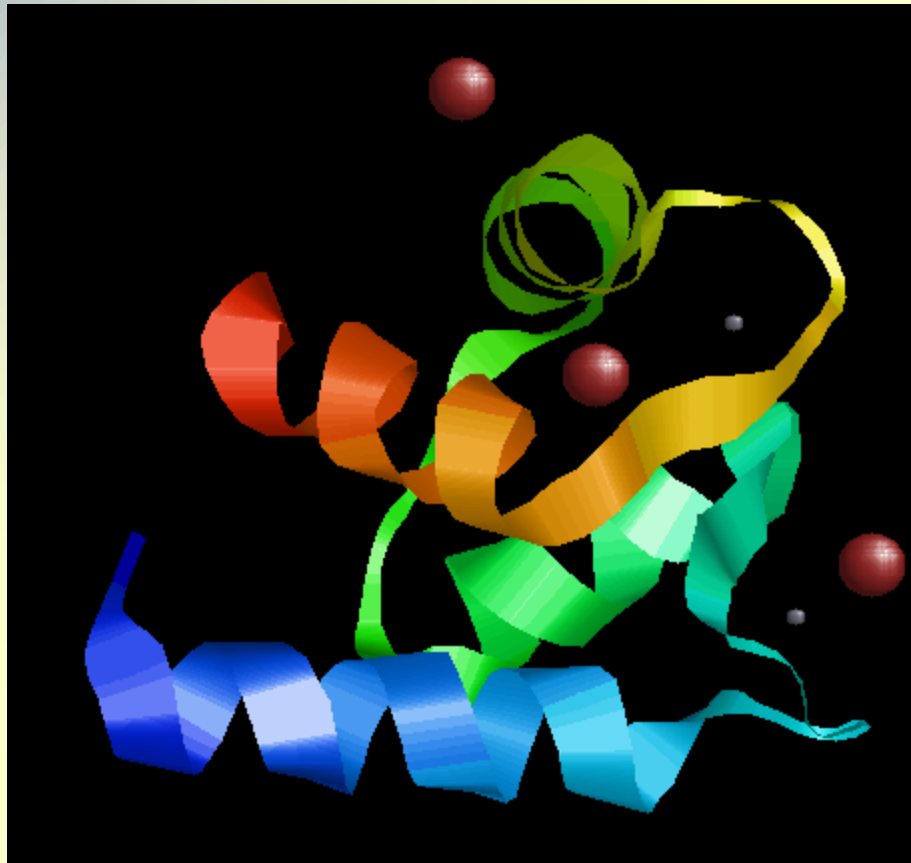


«EF-hands» - is a structural motif for calcium ions binding by proteins



The fragment of N-terminus of human calmodulin with calcium ions

Zinc ions also bind the protein, but in the other sites than calcium ions, unlike manganese ions



The fragment of N-terminus of human calmodulin with zinc and manganese ions

Calmodulin changes its conformation due to the calcium ions binding, even though the concentration of Ca^{2+} is 1000 lower than the concentration of Mg^{2+}



The fragment of N-terminus of human calmodulin with magnesium ions

Isomorphism of Ca^{2+} and Sr^{2+}

- $[\text{Ca}_{10}(\text{PO}_4)_6](\text{OH})_2$ – hydroxyapatite
- $[\text{Ca}_{10}(\text{PO}_4)_6]\text{CO}_3$ – carboapatite
- Isomorphism — is the ability of one type of ions to replace other type of ions in compounds
- Calcium and strontium have the same type of crystal lattice, the same charge, similar chemical properties

- So, strontium can be accumulated in bones. Radioactive strontium (^{90}Sr) is a beta emitter with a half-life of 29 years. Bone marrow is the main target for ^{90}Sr radiation. The worse consequence of its accumulation is leucosis if don't count radiation sickness.

Medicines containing calcium ions

- CaCl_2 – antiallergic, hemostatic
- CaCO_3 – antacid, antiulcerous
- Lactate, pangamate, pantetonate, gluconate of calcium are antiallergic, hemostatic medicines that also compensate the deficiency of calcium

Gypsum

- $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ – gypsum powder;
- $2(\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}) + 3 \text{H}_2\text{O} \rightarrow 2 (\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$



Test reactions for barium salts

Compounds of barium turn the color of the flame to yellow-green



Test reactions for BaSO₄

- First insoluble barium sulfate must be boiled with Na₂CO₃:
- $\text{BaSO}_4 \downarrow + \text{Na}_2\text{CO}_3 \rightarrow \text{BaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$
- The precipitate then must be filtered and dissolved in HCl solution.
- After that one can test the presence of Ba²⁺ cations in the solution with Na₂SO₄
- The test of purity (whether there is BaCO₃ in the sample) is performed with acetic acid. BaSO₄ must be filtered. Then the presence of barium cations must be checked in the solution.

The usage of compounds containing s^1 and s^2 elements in pharmacy

- $K_3[Fe(CN)_6]$ – test for Fe^{2+} ;
- $K_4[Fe(CN)_6]$ – test for Zn^{2+} and Cu^{2+} ;
- Na_2HPO_4 – test for Mg^{2+} ;
- $Na_3[Co(NO_2)_6]$ – test for K^+ ;
- $Na_2S_2O_3$ – quantitative analysis of I_2 ;
- $KMnO_4$ – quantitative analysis of Fe^{2+} ;
- $Na_2B_4O_7$ – quantitative analysis of HCl ;
- $CaCl_2$ – test for citrate (at high temperature);
- $BaCl_2$ – test for sulfate ions

**Thank you for
listening!**