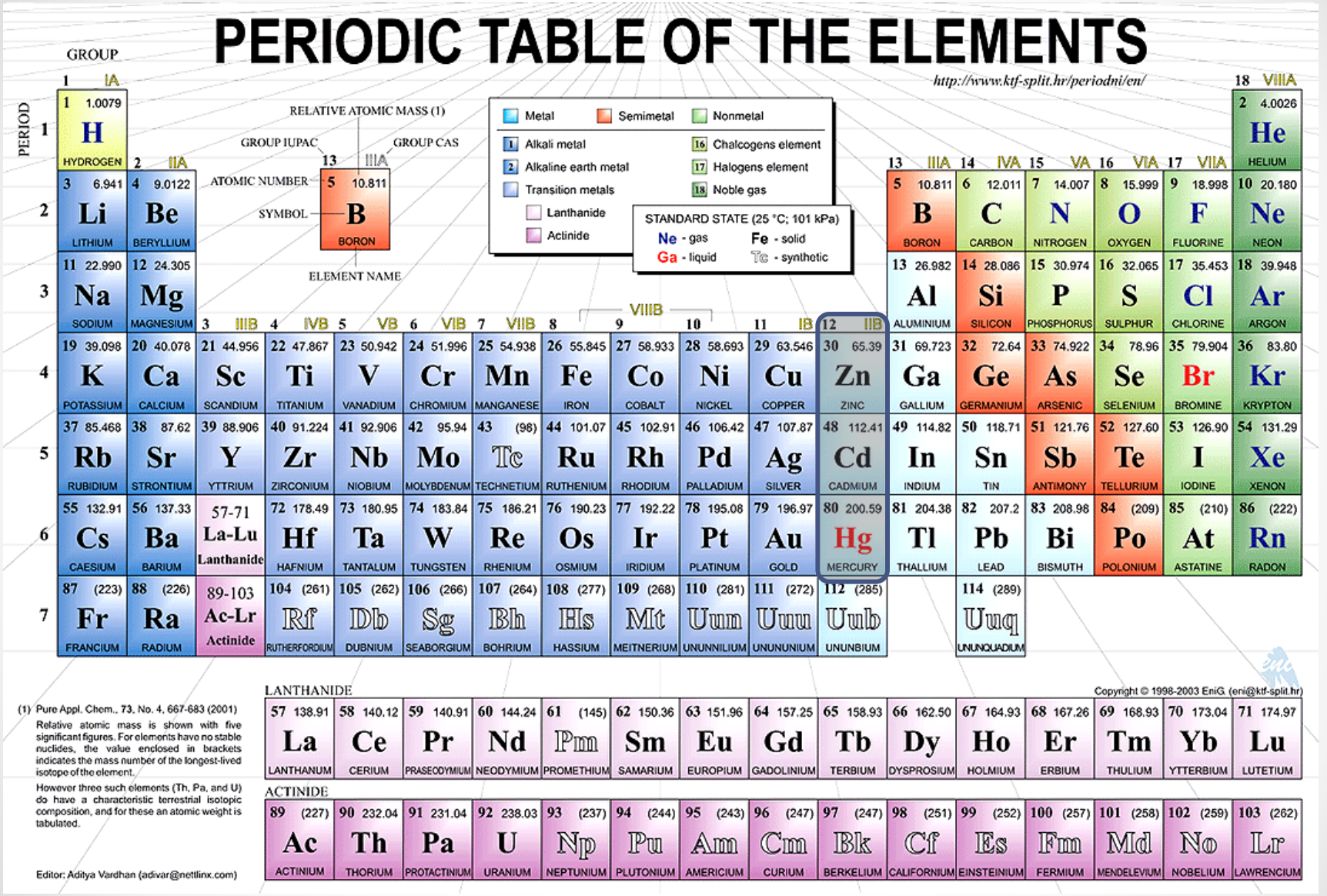
Chemistry of elements from group IIB

Lecture 7

The plan of the lecture

- Overall characteristic of elements from II B group
- Natural resources
- Chemical properties of metals from II B group and their compounds
- Biological roles of zinc
- The toxicity of mercury and cadmium
- The usage of compounds of IIB group elements in medicine


PERIODIC TABLE OF THE ELEMENTS
http://www.ktf-split.hr/periodni/en/
GROUP
PERIOD
RELATIVE ATOMIC MASS (1)
GROUP IUPAC
GROUP CAS
ATOMIC NUMBER
SYMBOL
ELEMENT NAME
Metal
Semimetal
Nonmetal
Alkali metal
Alkaline earth metal
Transition metals
Lanthanide
Actinide
Chalcogens element
Halogens element
Noble gas
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Ga - liquid
Fe - solid
Tc - synthetic
57-71 La-Lu Lanthanide
89-103 Ac-Lr Actinide
LANTHANIDE
ACTINIDE
(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have 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.
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The old version of the periodic table

Overall characteristic of the elements from IIB group

II B

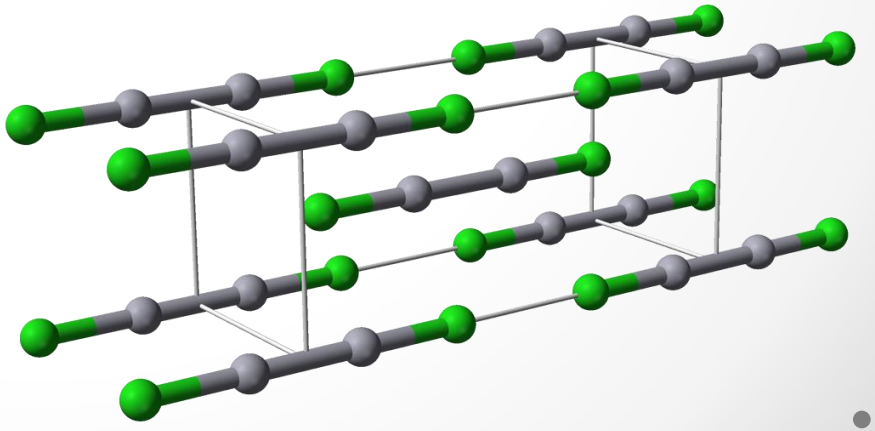
n = 4 **Zn** $^{65}_{30}$ **$ns^2(n-1)d^{10}$; outer shell 2ē**
preouter shell 18 ē

n = 5 **Cd** $^{112}_{48}$ **There are no unpaired electrons**

n = 6 **Hg** $^{201}_{80}$

Zn and Cd have the constant oxidation state of+2;
Hg can be in both +2 and +1 oxidation states

Cl-Hg-Hg-Cl = Hg_2Cl_2



Some physical and chemical parameters

II B: **Zn** **Cd** **Hg (liquid)**

1) Density (g/ml) — increases →

2) Atomic radius — < ≈ → increases

3) Electronegativity — 1.6 ≈ 1.7 < 1.9 → increases

4) Metallic properties — decrease ←

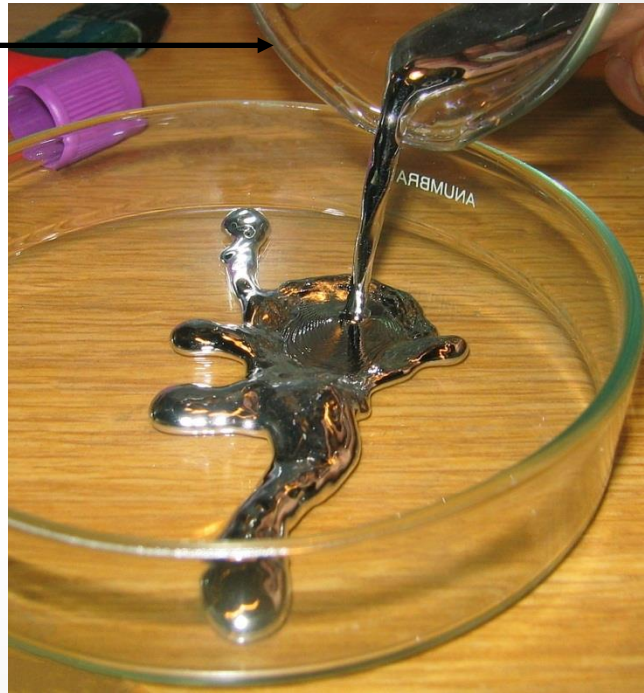
5) Chemical activity — decreases ←

6) Energy of ionuzation (kJ/mol) ≈ < → увеличивается

7) Standard electrode potential, B;

$E^0(Me^{2+}/Me^0)$ - 0,76 < - 0,402 < +0,85 (after H) → increases

8) $t_{melting,}$ ^0C → decreases



All metals from IIB group have low temperatures of melting, Mercury is liquid in standard conditions

Natural resources

ZnS wurtsite, sfalerite;

CdS greenokit;

HgS vermilion;

$ZnCO_3$ galmoy;

Mercury can sometimes be found as a pure element in nature

Chemical properties of pure elements

1) $2Zn + O_2 = 2ZnO$

2) Mercury can react with sulfur even at room temperature

$Hg + S = HgS$

This reaction is used to bind small amounts of mercury

Zn and Cd at ↑**t** form binary compounds with many nonmetals like **S, Se, F_2, P, As**

3) Halides are formed in reactions of group IIB metals with halogens (Cl_2, Br_2, I_2)

$Zn + Br_2 = ZnBr_2$ at room **t**

p-p

$Cd + Cl_2 = CdCl_2$ at high **t**

Hg forms two types of halides

70^0C $Hg + Cl_2 = HgCl_2$ mercury II chloride,

corrosive sublimate, highly toxic

250^0C $Hg + Cl_2 = Hg_2Cl_2$ mercury I chloride, **calomel,**

(Cl – Hg – Hg – Cl) less toxic than $HgCl_2$

$Hg + I_2 = HgI_2$ at room **t**

4) On the air **Zn and Cd** are slowly oxidized, they are covered by a protective oxide level

$2Zn + O_2 + 2H_2O = 2Zn(OH)_2$

$2Zn + O_2 + CO_2 + H_2O = (ZnOH)_2CO_3$

$ZnCO_3 \cdot Zn(OH)_2$

5) In normal conditions **Zn and Cd** cannot react with H_2O, while at high t° they form corresponding oxides.

$$Zn + H_2O = ZnO + H_2\uparrow$$

$$Cd + H_2O = CdO + H_2\uparrow$$

At very high t°

$$Cd + 2H_2O = Cd(OH)_2 + H_2\uparrow$$

Hg cannot react with H_2O

6) **Zn and Cd** are oxidized by "nonoxidizing" acids:

$$Zn + 2CH_3COOH = (CH_3COO)_2Zn + H_2\uparrow$$

Hg cannot react with such acids

7) Group IIB metals can be oxidized by H_2SO_4conc. and HNO_3.

The set of the products of reduction of oxidizing acids depends on their concentration and the nature of a metal.

$$4Zn + 5H_2SO_4(conc.) = 4ZnSO_4 + H_2S\uparrow + 4H_2O$$

$$4Zn + 10HNO_3(very\ dilute) = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Hg + 2H_2SO_4(conc.) = HgSO_4 + SO_2\uparrow + 2H_2O$$

$$6Hg + 8HNO_3(dilute) = 3Hg_2(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$3Hg + 8HNO_3(average\ conc.) = 3Hg(NO_3)_2 + 2NO\uparrow + 4H_2O$$

$$Hg + 4HNO_3\ (high\ conc.) = Hg(NO_3)_2 + 2NO_2\uparrow + 2H_2O$$

Reactions of zinc and copper with sulfuric acid

8) **Zn** can be dissolved in alkalis:

$$Zn + 2H_2O + 2OH^- = [Zn(OH)_4]^{2-} + H_2\uparrow$$

9) **Zn** can be oxidized by a water solution of ammonia in the absence of oxygen:

$$Zn + 4NH_3 + 2H_2O = [Zn(NH_3)_4](OH)_2 + H_2\uparrow$$

«Tin hedgehog»

$$SnCl_2 + Zn \rightarrow ZnCl_2 + Sn$$

Properties of Zn, Cd and Hg compounds

	Oxidation state	Oxides		Hydroxides		Salts	
		Formula	Acid-base properties	Formula	name	Formula	name
Zn	+2	ZnO white	Amphoteric	$Zn(OH)_2$	Zinc hydroxide	Zn^{2+}	Salts of zinc
				H_2ZnO_2	"Zinc acid"	ZnO_2^{2-} (t)	zincates
				$H_2[Zn(OH)_4]$ $Zn(OH)_2 \cdot 2H_2O$	Hydrogen tetrahydroxyzincate	$[Zn(OH)_4]^{2-}$ (p-p)	tetrahydroxyzincates

Cd	**+2**	**CdO** **brown**	**Amphoteric, but mostly basic**	**$Cd(OH)_2$** **H_2CdO_2**	**Cadmium hydroxide** **Cadmic acid**	**Cd^{2+}** **CdO_2^{2-}** **$[Cd(OH)_6]^{4-}$** ***In an alkali solution of a high concentration***	**Cadmium salts** **Cadmates** **hexahydroxycadmates**
Hg	**+1** **+2**	**Hg_2O** **black** **HgO** **yellow or red**	**basic** **basic**			**Hg_2^{2+}** **Hg^{2+}**	**Mercury I salts** **Mercury II salts**

Amphoteric properties

In water solution: $ZnO + 2H^+ = Zn^{2+} + H_2O$

In water solution: $ZnO + 2OH^- + H_2O = [Zn(OH)_4]^{2-}$

In the melt: $ZnO + 2NaOH = Na_2ZnO_2 + H_2O$

In water solution: $Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O$

In water solution: $Zn(OH)_2 + 2OH^- = [Zn(OH)_4]^{2-}$

In the melt: $Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$

Amphotericity of $Zn(OH)_2$

Weak amphoteric properties of cadmium hydroxide

$$Cd(OH)_2 + 4NaOH = Na_4[Cd(OH)_6]$$

in highly concentrated alkali

This complex decomposes in dilute solutions

CdO + concentrated alkali solution ≠

In the melt there will be cadmate:

$$Cd(OH)_2 + 4KOH \overset{t}{=} K_2CdO_2 + 2H_2O$$

Thermal instability of hydroxides:

$$Zn(OH)_2 \xrightarrow{t > 100^0C} ZnO + H_2O$$

$$Cd(OH)_2 \xrightarrow{t > 300^0C} CdO + H_2O$$

$$Hg(OH)_2 \longrightarrow HgO + H_2O$$

Mercury hydroxide decomposes immediately after the formation.

In basic medium salts of mercury I and II form mercury I and mercury II oxide, subsequently: $Hg_2O\downarrow$ *black-brown* or $HgO\downarrow$ *yellow*

Sample: $Hg(NO_3)_2 + 2NaOH = HgO\downarrow + 2NaNO_3 + H_2O$

Oxides of mercury are instable at high temperature:

$$2HgO \overset{t}{=} 2Hg + O_2$$

$$2Hg_2O \overset{t}{=} 4Hg + O_2$$

Hydroxides of zinc and cadmium are weak bases.
Salts of zinc and cadmium are hydrolyzed.
pH<7 in their water solutions.

Amphotericity of zinc and cadmium may be described as the ability of Zn^{2+} and Cd^{2+} to exist in both cationic $[Me^{2+}(H_2O)_n]^{2+}$ and anionic forms $[Me^{2+}(OH)_n]^{(n-2)-}$ in water solutions.

Coordination number is 4 or 6.

Mercury (II) cation forms an instable aquatic complex

$$[Hg(H_2O)_2]^{2+}$$

(addition of HNO_3 prevents hydrolysis of mercury (II) salts)

Zinc usually demonstrates the coordination number of 4 (complexes are tetrahedral).

Cadmium usually demonstrates the coordination number of six (complexes are octahedral).

Mercury may demonstrate coordination number of 4 or 6.

$$Zn(OH)_2 + 4NH_3 = [Zn(NH_3)_4](OH)_2$$

$$CdCl_2 + 6NH_4OH = [Cd(NH_3)_6]Cl_2 + 6H_2O$$

Stability of amminocomplexes decreases from zinc to mercury.

Amminocomplexes of mercury are formed *only in the presence of ammonium salts. In the absence of ammonium salts amides of mercury are formed.*

$$HgCl_2 + 2NH_3 = Hg(NH_2)Cl\downarrow + NH_4Cl$$

Mercury (II) amidochloride

$$Hg_2Cl_2 + 2NH_3 = Hg(NH_2)Cl\downarrow + NH_4Cl + Hg\downarrow$$

Mercury (I) amidochloride

Both reactions are used in chemical analysis to detect Hg^{2+} and Hg_2^{2+} cations.

Stability of complexes with halide ions increases from zinc to mercury and from chloride to iodide.

$K_2[ZnI_4]$ – is instable and behaves as a double salt $ZnI_2 \cdot 2KI$.

$$CdS\downarrow + 4NaCl = Na_2[CdCl_4] + Na_2S$$

yellow — conc. — more stable

$K_{inst.} = 9.3 \cdot 10^{-3}$

High stability of $[HgI_4]^{2-}$

($K_{inst.} = 1.5 \cdot 10^{-30}$) *is the cause of the possibility of the dissolving of mercury in hydroiodic acid*

$$Hg + 4HI \rightarrow H_2[HgI_4] + H_2\uparrow$$

$$HgS\downarrow + 4KI \rightarrow K_2[HgI_4] + K_2S$$

black excess potassium tetraiodohydrargyrate (II)

($K_{inst.} = 1.5 \cdot 10^{-30}$)

$K_2[HgI_4]$ + KOH – is the Nessler reactant to detect NH_3

(red-brown precipitate is formed)

Chlorides, bromides, iodides of cadmium and mercury form anionic autocomplexes in solutions.

$Cd[CdI_4]$; $Cd[CdI_3]_2$; $Cd[CdCl_4]$; $Hg[HgCl_4]$; $Hg[HgI_3]_2$

$2CdBr_2 = Cd[CdBr_4]$; $3HgI_2 = Hg[HgI_3]_2$

Zinc, cadmium and mercury form stable cyanocomplexes

$$Cd(OH)_2 + 4KCN = K_2[Cd(CN)_4] + 2KOH$$

$K_{inst.}[Zn(CN)_4]^{2-} = 1.3 \cdot 10^{-17}$; $K_{inst.}[Cd(CN)_4]^{2-} = 1.4 \cdot 10^{-19}$; $K_{inst.}[Hg(CN)_4]^{2-} = 4.0 \cdot 10^{-42}$.

Stability of cyanocomplexes increases from zinc to mercury.

Mercury is much different from Zn and Cd both in physical and chemical properties.

Mercury dissolves many metals, and forms solid and liquid alloys – amalgams.

Interestingly, iron cannot form an amalgam with mercury.

Because of this reason mercury is transported in iron containers.

Halides and cyanide of mercury

($HgCl_2$, $HgBr_2$, HgI_2, $Hg(CN)_2$) are *molecular*, and not ionic compounds. These linear molecules have mercury in sp-hybridization and strong covalent bonds between Hg and C. These compounds are *nonelectrolytes* (their solutions cannot conduct electricity), but they are soluble in nonpolar solvents.

One of the few mercury II salts soluble in water is mercury (II) nitrate – *$Hg(NO_3)_2$*. This salt can be completely hydrolyzed in water solution:

or

$$\left.\begin{array}{l} Hg(NO_3)_2 + H_2O \rightarrow HgOHNO_3\downarrow + HNO_3 \\ Hg(NO_3)_2 + H_2O \rightarrow HgO\downarrow + 2HNO_3 \end{array}\right\} \text{pH} < 7$$

to stop hydrolysis you should use

1) + HNO_3 **for** $Hg(NO_3)_2$

2) + Hg **for** $Hg_2(NO_3)_2$

to prevent the disproportioning

Compounds of mercury (I) are less stable than compounds of mercury (II), and they are prone to disproportioning:

$$Hg \rightarrow Hg + Hg$$

$$Hg_2Cl_2 \rightarrow HgCl_2 + Hg$$

$$Hg_2(CN)_2 \rightarrow Hg(CN)_2 + Hg$$

$$Hg_2S \rightarrow HgS + Hg$$

Salts of mercury (I) can act as both reducers and oxidizers

$$2Hg_2(NO_3)_2 + O_2 + 4HNO_3 \rightarrow 4Hg(NO_3)_2 + 2H_2O$$

reducer

$$Hg_2(NO_3)_2 + Zn \rightarrow Zn(NO_3)_2 + 2Hg\downarrow$$

oxidizer

Sublimate ($HgCl_2$) is soluble in water, alcohol, ethers and carbon sulfide

Hydrolysis: $HgCl_2 + H_2O \rightarrow HgOHCl\downarrow + HCl$

$HgCl_2 + H_2O \rightarrow HgO\downarrow + 2HCl$

Production:

$$HgSO_4 + 2NaCl \overset{t}{=} Na_2SO_4 + HgCl_2$$

sublimate

$$HgCl_2 \xrightarrow{t} Hg + Cl_2$$

$$2HgCl_2 + H_2[SnCl_4] = Hg_2Cl_2 + H_2[SnCl_6]$$

calomel

Biological roles of zinc and the usage of its compounds in medicine

The level of elements in the human body

1.8-2.3 g Zn – absolutely essential element → daily dosage is 8-22 mg

50 mg Cd – toxic

13 mg Hg – highly toxic

Zn – is a co-factor of many enzymes.

Some samples of such metalloenzymes:

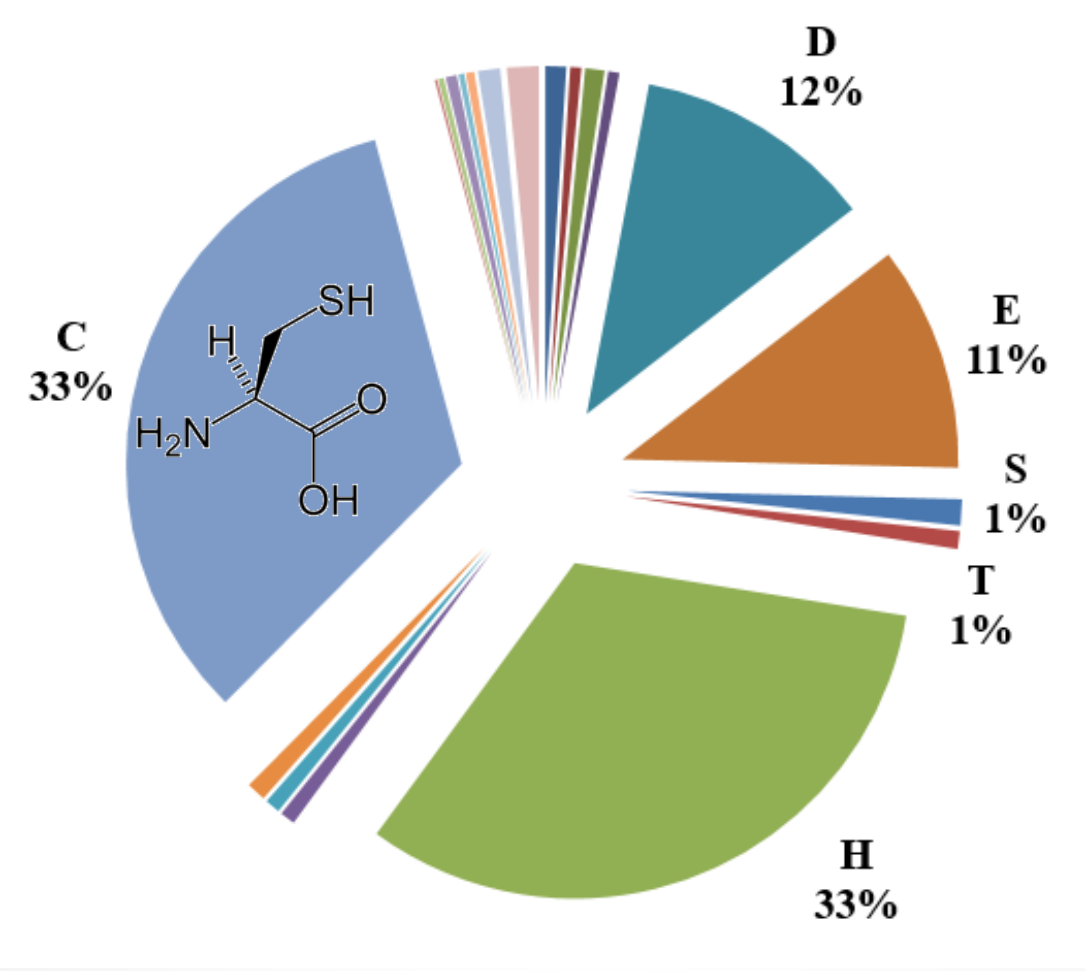
1) **Carbonic anhydrase:** $CO_2 + H_2O \rightarrow HCO_3^- + H^+$

This enzyme makes the velocity of the process 10^7 times faster.

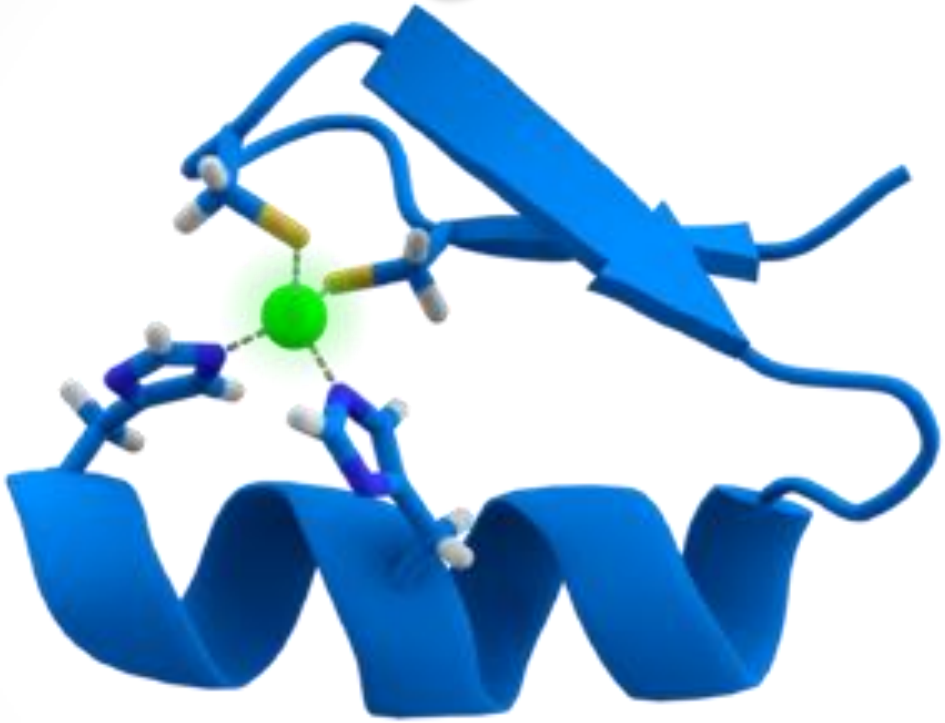
2) **Carboxypeptidase: hydrolyzes peptide bonds starting from C-terminus of the polypeptide chain.**

3) **Alcohol dehydrogenase catalyzes the process of oxidation of alcohols to aldehydes.**

The percentage of amino acids binding Zn^{2+} in proteins

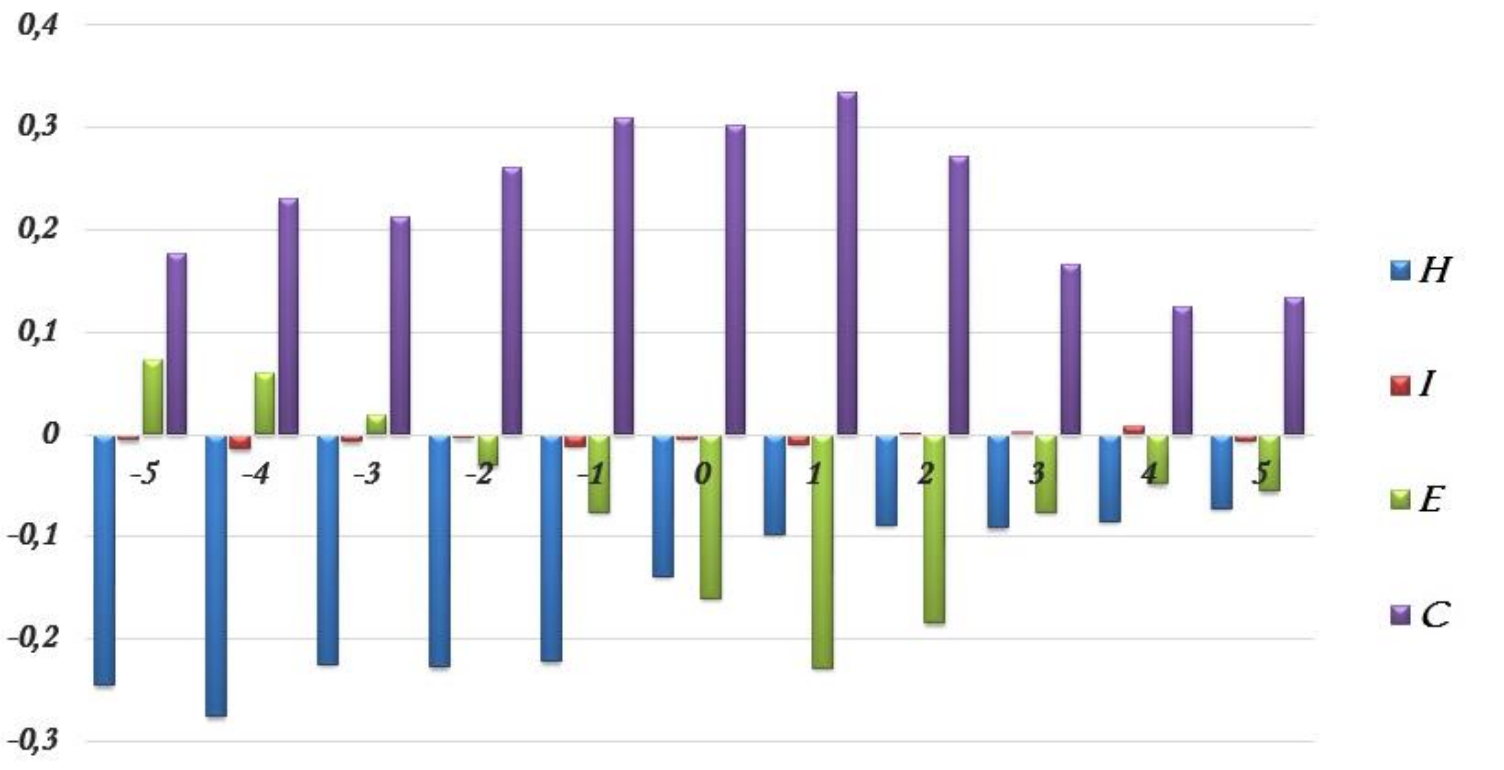


Zinc finger domain



X_2-Cys-$X_{2,4}$-Cys-X_{12}-His-$X_{3,4,5}$-His

Just 35.51% of coordination spheres for zinc really contain cysteine residues



Zn^{2+} – **makes the action of insulin longer;**

- **protects –SH groups from the oxidation;**
- **is necessary for calcification of bones and the healing of wounds;**
- **is necessary for the reception of taste;**
- **is necessary for gene expression regulation.**

Zinc-deficiency is associated with numerous complications

For example:

- **anemia;**
- **Prasad's disease – growth defect (dwarf);**
- **insufficiency of sexual development**

Cd and Hg – are poisonous

Some properties of cadmium and mercury make them especially dangerous:

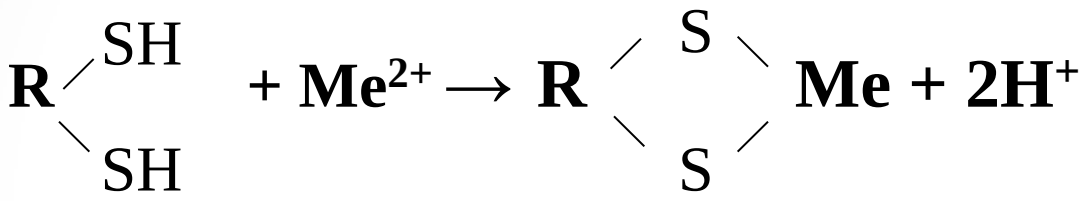
1) **Their compounds can get in the organism via both digestive system and lungs;**
2) **They are accumulated in the organism, since their half-clearance periods are too long (around 25 years for Cadmium)**

3) Mercury and cadmium are antimetabolites of zinc and calcium – means they disturb the function of numerous enzymes;

4) Liver, kidneys and brain are the main targets for mercury and cadmium compounds;

5) Compounds of mercury and cadmium can get through placenta.

Example: they block – SH – groups of proteins



Special names for intoxication: *cadmiosys and mercuriosys*

Cadmiosys: **– Itai-itai disease - osteomalation;**
– nephropathy;
– neurotoxic syndrome.

Mercuriosys: **– «Minamata disease» – (CH_3HgCl) –methylmercury accumulates in plankton, in mollusks, in fish, and then in human**

and causes mental dysfunctions (1956).

– $HgCl_2$ easily gets in adipose tissue. «Sublimic kidney» – causes anuria; and low osmotic resistance of red blood cells.

Hg and mercury vapor – causes the mad hatter disease.

The usage in medicine

Zn – to compensate zinc defficiency:

~ per os: sulfate
gluconate
aspartate
polyvitamins + microelements

~ on a skin: antiseptic, antiinflammatory

ZnO: zinc ointment; suppositories

0,25% water solution of $ZnSO_4$ is used as eye drops.

$ZnCl_2$ – is used to remove papilomas.

Cd – is not used in medicine, while previously it was used to kill helmets in animals

Hg – HgO **yellow mercury ointment**
$HgNH_2Cl$ **white mercury ointment**
} ***used previously to make skin pale***

Antiseptics

- $Hg(CN)_2 \cdot HgO$ **mercury (II) oxycyanide – to treat syphilis**
- $HgCl_2$ **solutions 1:1000 were used for desinfection**

Hg_2Cl_2 **– was used as laxative even in XX century.**

Amalgams were used in dentistry.

Thank you for listening!