Chemical properties of the elements from IB group and from the platinum family

The plan of the lecture

1.Overall characteristic of elements from IB group

2.Natural resources of elements from IB group

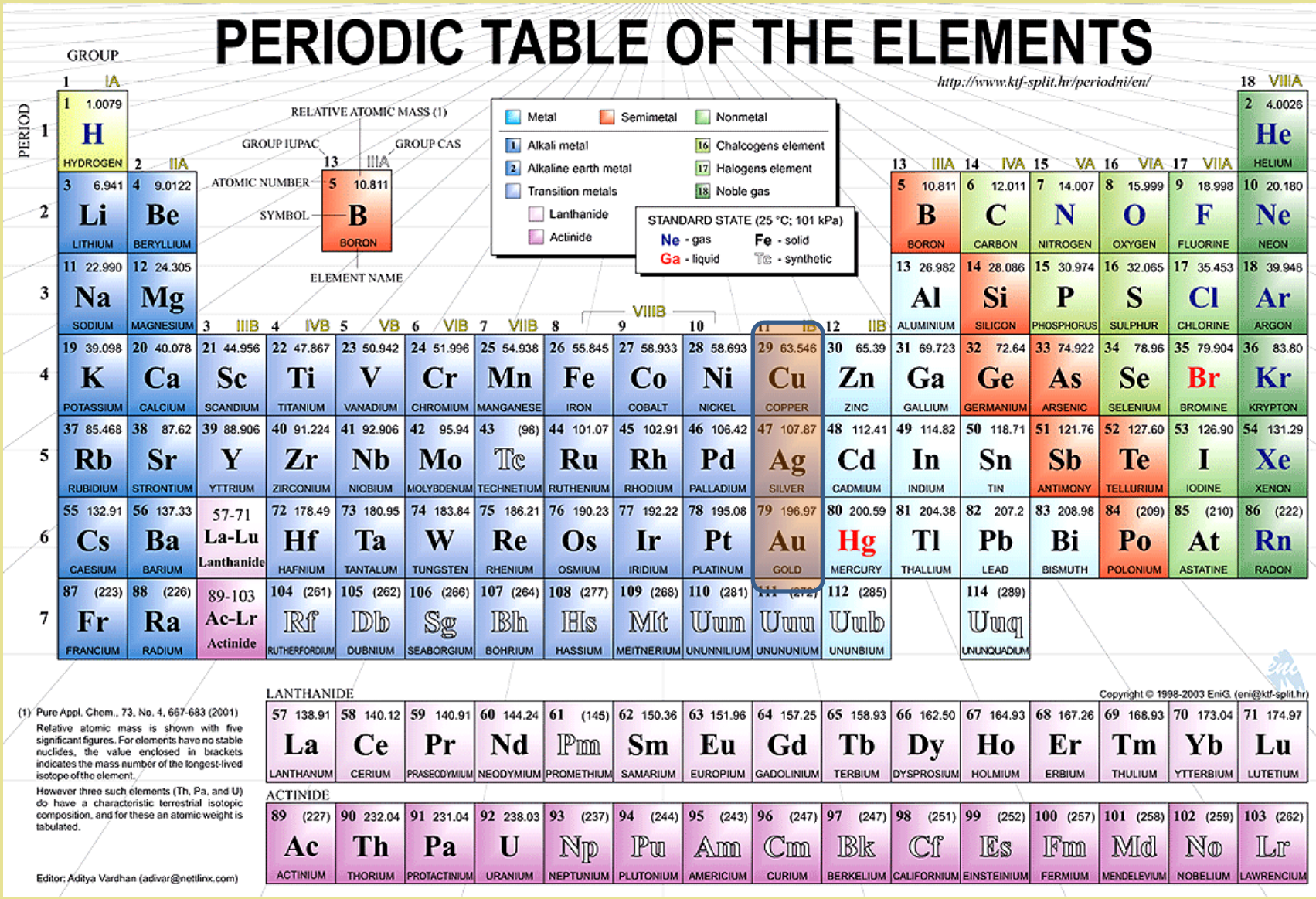
3.Physical and chemical properties of copper, silver and gold

4.Main compounds of copper, silver and gold.

5.The usage of copper, silver and gold in medicine.

6. Properties of metals from platinum family.

PERIODIC TABLE OF THE ELEMENTS



(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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Old version of the periodic table

Overall characteristic of elements from IB group

- Electron configuration:
- Cu: [Ar] $4s^1$ $3d^{10}$
- Ag: [Kr] $5s^1$ $4d^{10}$
- Au: [Xe] $6s^1$ $4f^{14}$ $5d^{10}$
- Copper, silver and, especially, gold are very inert. Because of this reason they can be found as elements in nature.
- However, they are prone to form complexes.

2.Natural resources of elements from IB group

- **<u>Gold</u>** is thought to be the first metal a mankind get familiar with. It happened about 5 000 years B.C.

In nature gold exists as:

- Pure chemical element;
- Electrum (Au + 15 – 50% Ag);
- Sulfides, arsenides, tellurides.

«Philosopher's stone»

- There was a dream of ancient alchemists about a substance called "Philosopher's stone" that can turn metals to gold.
- In 1947 35 mcg of gold have been produced in a nucleic reaction from mercury.
- However, such a "transmutation" cannot be used in commerce. The price of that process is too expensive.

2.Natural resources of elements from IB group

- **Silver** is known for about 5 000 years B.C.
- In nature silver can be found as:
- Pure chemical element;
- Electrum (Au + 15 – 50% Ag);
- Argenite – Ag_2S;
- Kerargirite – AgCl

2.Natural resources of elements from IB subgroup

- **Copper** is known since 3 000 years B.C. There were ancient mining camps on the island Cyprus.

Natural minerals are:

- Copper iron (II) sulfide $CuFeS_2$;
- Halkozine – Cu_2S; covelline – CuS;
- Copprite – Cu_2O;
- Azurite – $Cu_3(CO_3)_2(OH)_2$ or $2CuCO_3 \cdot Cu(OH)_2$;
- Malachite – $Cu_2CO_3(OH)_2$
  or $(CuOH)_2CO_3$
  or $CuCO_3 \cdot Cu(OH)_2$;
- Copper as a pure chemical element is rare in nature.

Physical and chemical properties of copper

- Copper is an orange-pink plastic metal. It is covered by a layer of copper (II) oxide on the open air. That layer changes the overall color of copper to yellow-red.
- With the coarse of time

  copper is covering up by a layer

  of green hydroxycarbonate:
- $2Cu + H_2O + CO_2 + O_2 \rightarrow (CuOH)_2CO_3$

Physical and chemical properties of silver

- Pure **silver** is very plastic white metal (the coefficient of the reflection of light is close to 100 %). It is the best known conductor of electricity. With the coarse of time that metal is losing its reflecting ability because of the corrosion by hydrogen sulfide in the presence of oxygen. Silver sulfide has a black color.
- $4Ag + 2H_2S + O_2 \rightarrow 2Ag_2S + 2H_2O$

Physical and chemical properties of gold

- **Gold** is a soft and plastic yellow metal.
- In normal conditions it cannot react with the most of the acids, as well as with oxygen. Because of this reason gold is so expensive. Indeed, other metals can be easily destroyed by acids and bases.
- However, gold can easily react with reactants that can form a complex compound in the presence of oxygen. For example, gold can be dissolved in water solutions of cyanides in the presence of oxygen:
- $4Au + 8KCN + 2H_2O + O_2 \rightarrow 4K[Au(CN)_2] + 4KOH$
- $2K[Au(CN)_2] + Zn \rightarrow K_2[Zn(CN)_4] + 2Au\downarrow$

Chemical properties of copper

- $2Cu + O_2$ (400 – 500°C) → $2CuO$
- $4Cu + O_2$ (> 800°C) → $2Cu_2O$

- $Cu + S$ (t_1°) → CuS
- $2Cu + S$ (t_2° > t_1°) → Cu_2S

- $Cu + Cl_2 \rightarrow CuCl_2$

Reaction between copper and chlorine gas

Chemical properties of copper

- Dilute solutions of nonoxidizing acids and alkalis (in the absence of oxidizers) usually cannot react with copper.
- $Cu + 4HNO_3$ (conc.) → $Cu(NO_3)_2 + 2NO_2 + 2H_2O$
- $3Cu + 8HNO_3$ (40%) → $Cu(NO_3)_2 + 2NO + 4H_2O$
- $Cu + 2H_2SO_4$ (conc.) → $CuSO_4 + SO_2 + 2H_2O$
- $2Cu + 4HCl$(conc.) → $2H[CuCl_2] + H_2$
- $2Cu + 4HCl$(dilute) $+ O_2 → 2CuCl_2 + 2H_2O$
- $2Cu + H_2S → Cu_2S + H_2$
- $2Cu + 8NH_4OH + O_2 → 2[Cu(NH_3)_4](OH)_2 + 6H_2O$
- $2Cu + I_2 → 2CuI$ $((Cu^{2+} + 4I^- → 2CuI + I_2))$

Copper (I) oxide and hydroxide

- $Cu_2O + 4HCl \rightarrow 2H[CuCl_2] + H_2O$
- $CuOH + HCl \rightarrow CuCl\downarrow + H_2O$
- $Cu_2O + H_2SO_4 \rightarrow CuSO_4 + H_2O + Cu\downarrow$
- $Cu_2O + 2NaOH(conc.) \rightarrow 2Na[Cu(OH)_2]$
- $CuOH + NaOH(conc.) \rightarrow Na[Cu(OH)_2]$
- $Cu_2O + 4NH_3 + H_2O \rightarrow 2[Cu(NH_3)_2]OH$
- $CuOH + 2NH_3(aq.) \rightarrow [Cu(NH_3)_2]OH$
- $4CuOH + O_2 + 2H_2O \rightarrow 4Cu(OH)_2$

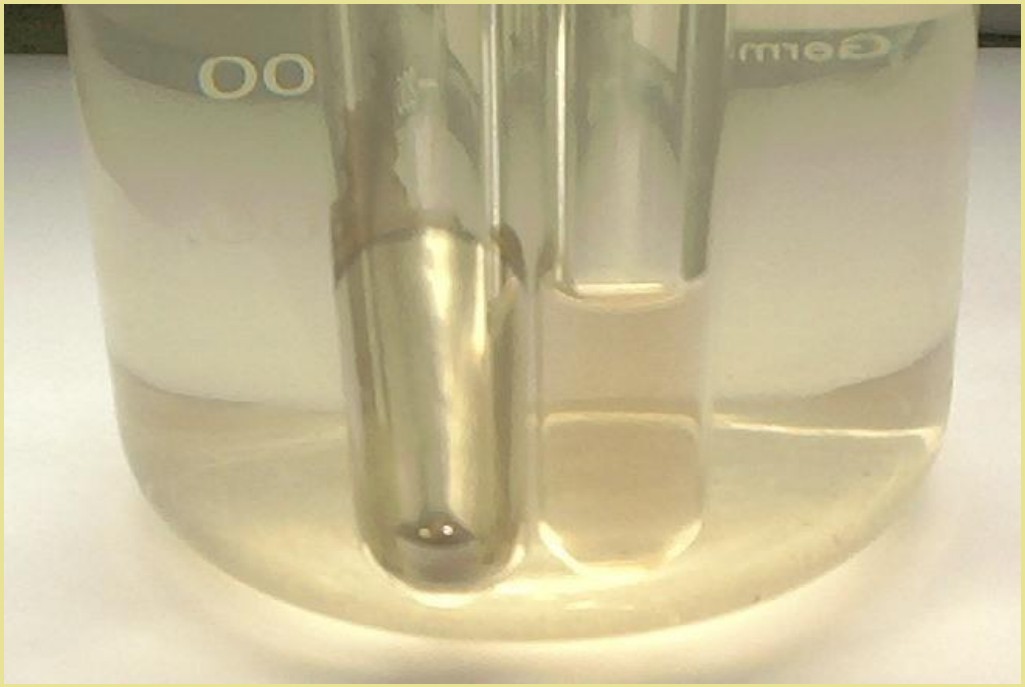
Salts of copper

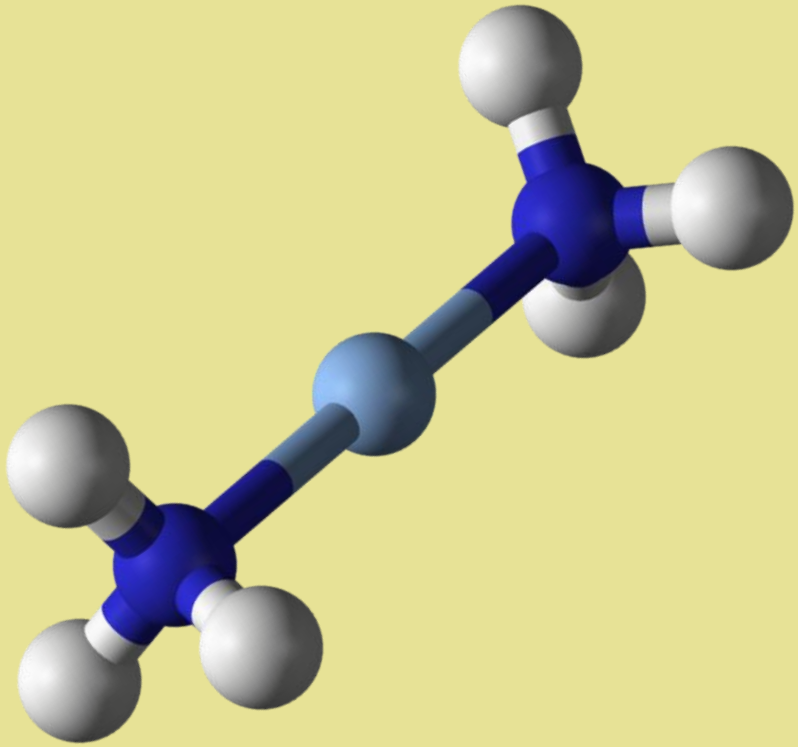
- $4CuCl + O_2 + 4HCl \rightarrow 4CuCl_2 + 2H_2O$
- $2CuCl\ (t°) \rightarrow 2Cu + CuCl_2$
- $CuSO_4\ (t°) \rightarrow Cu + CuSO_4$
- $CuCl + Cl_2 \rightarrow CuCl_2$
- $CuCl_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]Cl_2$
- $CuCl_2 + 2NaCl(conc.) \rightarrow Na_2[CuCl_4]$
- $2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + 2CuI + I_2$

Chemical properties of silver

- $2Ag + H_2S\ (t°) \rightarrow Ag_2S + H_2\uparrow$
- $2Ag + S\ (t°) \rightarrow Ag_2S$
- $2Ag + 2HI(aq)\ (t°) \rightarrow 2AgI + H_2\uparrow$
- $2Ag + 2HCl(g)\ (t°) \rightarrow 2AgCl + H_2\uparrow$
- $2Ag + 2H_2SO_4\ (conc.) \rightarrow Ag_2SO_4 + SO_2\uparrow + 2H_2O$
- $Ag + 2HNO_3\ (conc.) \rightarrow AgNO_3 + NO_2\uparrow + H_2O$
- $3Ag + 4HNO_3\ (dilute) \rightarrow 3AgNO_3 + NO\uparrow + 2H_2O$

Tollens' reactant





$AgNO_3 + NaOH \rightarrow AgOH + NaNO_3$

$2AgOH \rightarrow Ag_2O\downarrow + H_2O$

$Ag_2O + 4NH_3 + H_2O + 2NaNO_3 \rightarrow 2[Ag(NH_3)_2]NO_3 + 2NaOH$

$AgNO_3 + 2NH_3 \rightarrow [Ag(NH_3)_2]NO_3$

$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag\downarrow + 2NH_3$

$R\text{-}HC{=}O + 3OH^- - 2e^- \rightarrow R\text{-}COO^- + 2H_2O$

Test reactions for polyatomic alcohols and aldehydes with the fresh $Cu(OH)_2$

$$R\text{-}HC{=}O + 2Cu(OH)_2 \rightarrow R\text{-}HCOOH + Cu_2O\downarrow + 2H_2O$$

$AgNO_3$ as a reactant to reveal the presence of chlorides, bromides and iodides in water solutions

Chemical properties of gold

- Gold can be dissolved in ***selenic acid*** (but it cannot be dissolved in any other individual acid) at 200 °C:
- $2Au + 6H_2SeO_4 \rightarrow Au_2(SeO_4)_3 + 3H_2SeO_3 + 3H_2O$
- $2Au + 3Cl_2\ (200°C) \rightarrow 2AuCl_3$
- $2Au + 3Br_2 \rightarrow 2AuBr_3$
- $2Au + I_2 + 2KI \rightarrow 2K[AuI_2]$
- $Au + Cs \rightarrow CsAu$
- $2Au + 2HCl + 3Cl_2 \rightarrow 2H[AuCl_4]$

“Tsar’s vodka”

Tsar’s vodka (*Aqua Regia, Aqua Regis, A.R.*) — is the mixture of concentrated nitric HNO_3 (65-68 % by mass) and hydrochloric HCl (32-35 % by mass) acids, taken in the proportion of 1:3 by volume (mass ratio per pure acids is about 1:2)

“Tsar’s vodka”

- A mixture of numerous products forms when HCl reacts with HNO_3. Some of them are free radicals like atomic chlorine and NO.
- $3HCl + HNO_3 \rightarrow 2Cl\cdot + NOCl + 2H_2O$
- $NOCl \rightarrow NO + Cl\cdot$
- $2NO + O_2 \rightarrow 2NO_2$
- This mixture must be fresh to keep its oxidizing properties. One of the end products of the reactions in Tsar’s vodka is nitrogen dioxide that has a brown color.

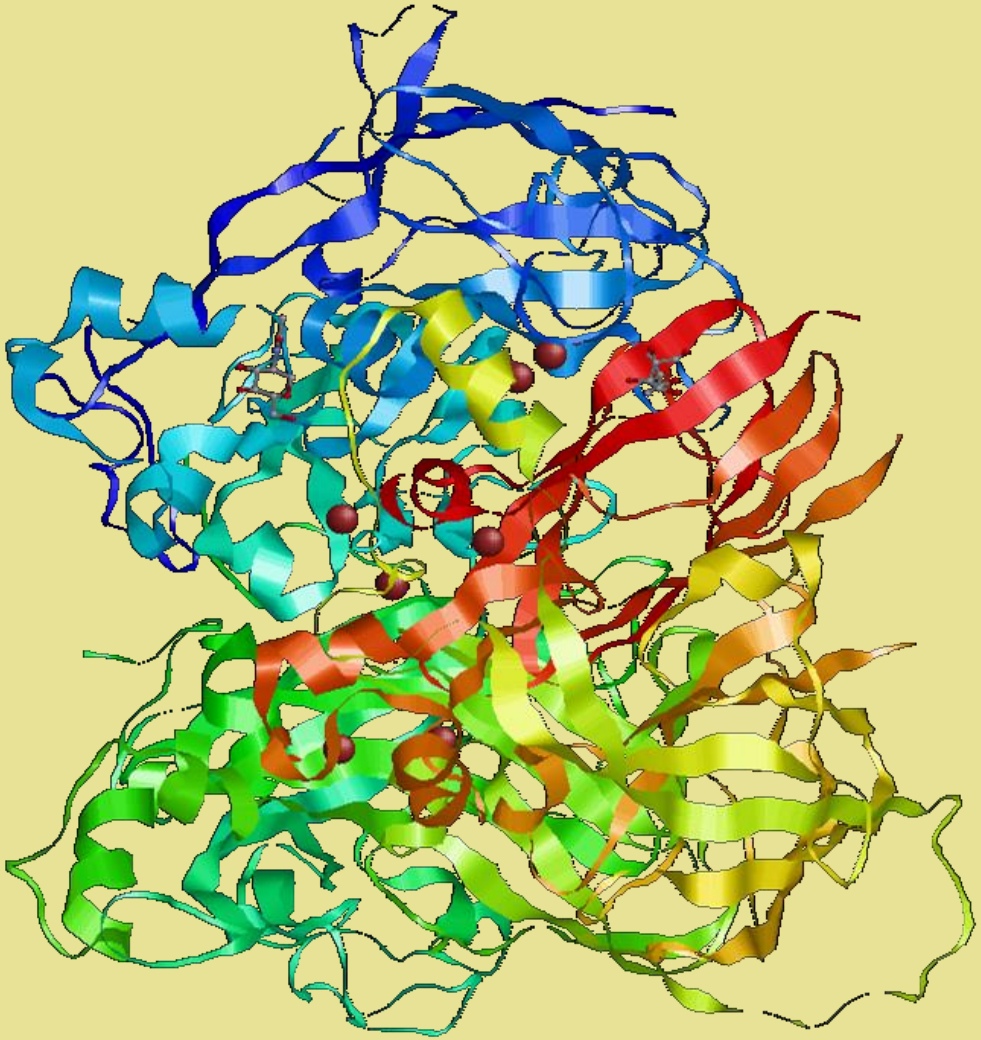
“Tsar’s vodka”

- $Au + 4HCl + HNO_3 \rightarrow H[AuCl_4] + NO\uparrow + 2H_2O$
- Silver cannot be dissolved in Tsar’s vodka because of the passivation by insoluble AgCl.
- $2[AuCl_4]^- + 3Fe^{2+} \rightarrow 3Fe^{3+} + 8Cl^- + 2Au\downarrow$
- $4[AuCl_4]^- + 3N_2H_4 \rightarrow 3N_2 + 12H^+ + 16Cl^- + 4Au\downarrow$

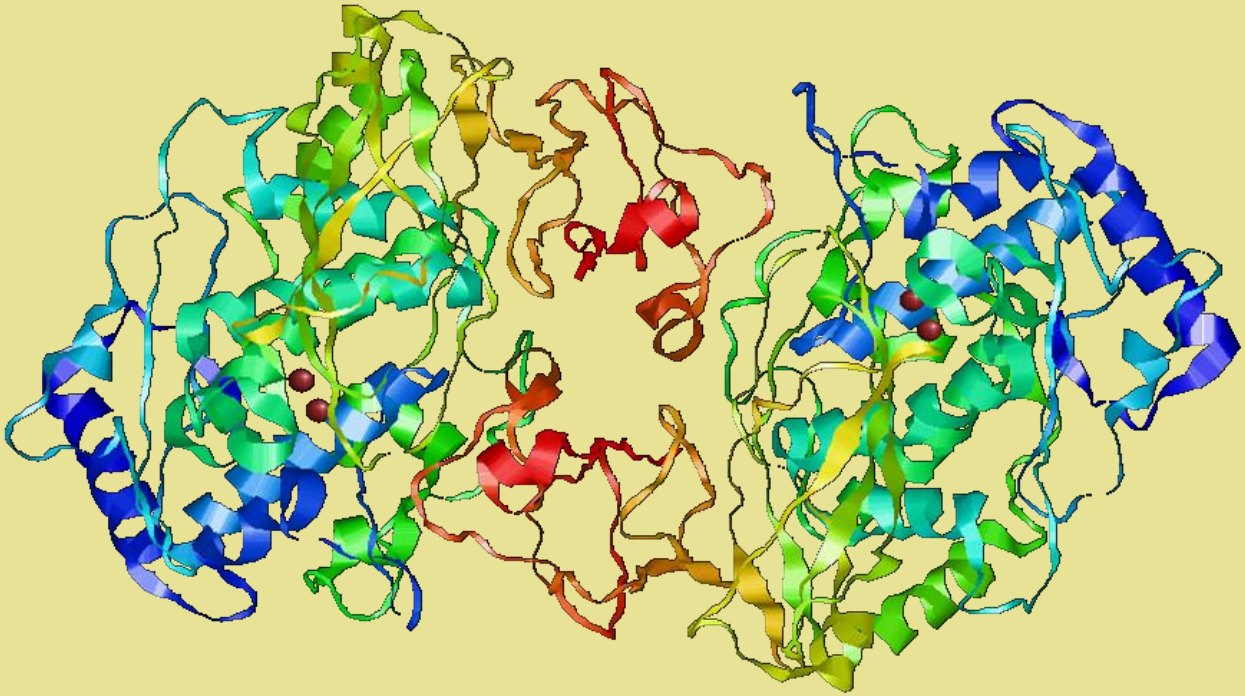
Biological roles of copper

- Copper is an essential element for all plants and animals. Copper is transported in blood by a specific protein that is called cerulloplasmin.
- Copper ions are co-factors for numerous enzymes including cytochrome c oxidase and superoxide dismutase.
- In blood of some mollusks and arthropoda oxygen is transported by hemocyanine. In that protein there are no porfirine rings, copper ions are coordinated by nitrogen atoms from histidines.

Cerulloplasmin



Hemocyanine



The usage of copper and its compounds in medicine

- In 2008 the fact of the existence of bactericide surface of copper has been officially confirmed in USA.
- Staphylococcus aureus with the resistance to multiple drugs (MRSA) is sensitive to copper and its alloys.
- Also copper can deactivate Influenza virus.

The usage of copper and its compounds in medicine

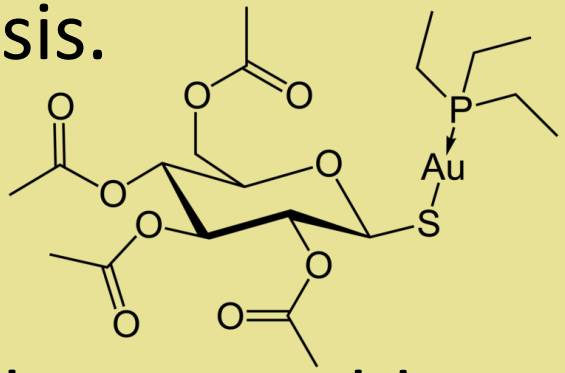
- $CuSO_4 \cdot 5H_2O$ – is an antiseptic (it can be found in eye drops, gastric lavage solutions)
- $CuSO_4$ – is a frequent component of vitamin and mineral complexes

The usage of silver and its compounds in medicine

- **Silver proteinate** – **collargol, protargol** – colloid silver – is the result of chemical reaction between silver oxide and proteins, such as BSA or casein. Silver ions are released slowly from these proteinates.

The usage of compounds of gold in medicine

- Organic compounds of gold (cryzanol and **auranofine**) are used in medicine with the aim to treat autoimmune diseases (including rheumatoid arthritis) and amebiasis.



- Compounds of gold are toxic, while pure gold is inert and cannot demonstrate its toxic properties.

The usage of gold in medicine

- Tooth crowns can be made from gold.

- **«Gold for drinking»** — is a colloid solution with a red color. It is still popular, even though it is inert. Ancient Chinese alchemists started to drink colloid gold solutions about 1 000 years B.C.

The chemistry of elements from the platinum family

1.Physical and chemical properties

These metals are shiny gray. Pd and Pt are soft; Ir is hard and durable; Os and Ru are fragile.

Pt – metals are inert.

These metals are resistant to corrosion in normal conditions. They can dissolve hydrogen.

Pd and Pt are frequently used as catalysts.

$Me \xrightarrow{O_2} RuO_2, IrO_2, Ir_2O_3, Rh_2O_3, PdO, PdO_2, PtO_2, OsO_4, RuO_4$

$Me \xrightarrow{F_2} RuF_6, RhF_6, PdF_3, IrF_6, PtF_6, OsF_7$

$Me \xrightarrow{Cl_2} RuCl_3, RhCl_3, PdCl_2, IrCl_3, OsCl_4, PtCl_4$

Pt metals **cannot react with HCl and diluted H_2SO_4 and HNO_3.**

$$Os + 8HNO_{3(conc.)} \rightarrow OsO_4 + 8NO_2\uparrow + 4H_2O$$

$$Pd + 2H_2SO_{4(conc.)} \xrightarrow{t} PdSO_4\downarrow + SO_2 + 2H_2O$$

$$Pd + 4HNO_{3(conc.)} \xrightarrow{t} Pd(NO_3)_2\downarrow + 2NO_2 + 2H_2O$$

Tsar's vodka reacts with those metals

$$2HNO_3 + 12HCl + 2Rh \rightarrow 2H_3[RhCl_6] + 2NO + 4H_2O$$

Fractioned state

$$4HNO_3 + 18HCl + 3Ir \rightarrow 3H_2[IrCl_6] + 4NO + 8H_2O$$

Fractioned state

$$4HNO_3 + 18HCl + 3Pt \xrightarrow{t} 3H_2[PtCl_6] + 4NO + 8H_2O$$

Hydroxides of platinum metals ($Me(OH)_2$, $Me(OH)_3$, $Me(OH)_4$) demonstrate weak basic or amphoteric properties.

$$Pd(OH)_2 + 2HCl \rightarrow PdCl_2 + 2H_2O$$

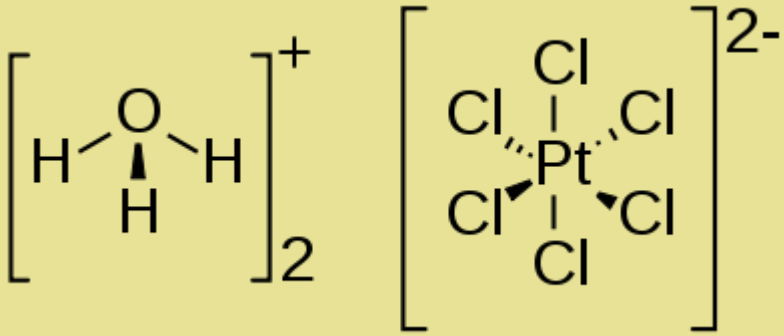
$$Pd(OH)_2 + 2NaOH \rightarrow Na_2[Pd(OH)_4]$$

$$Pt(OH)_4 + 2NaOH \rightarrow Na_2[Pt(OH)_6]$$

or $$PtO_2 \cdot 4H_2O + 2NaOH \rightarrow Na_2[Pt(OH)_6] + 2H_2O$$

$$Pt(OH)_4 + 6HCl \rightarrow H_2[PtCl_6] + 4H_2O$$

or $$PtO_2 \cdot 4H_2O + 6HCl \rightarrow H_2[PtCl_6] + 6H_2O$$



THE USAGE OF COMPOUNDS OF PLATINUM FAMILY ELEMENTS

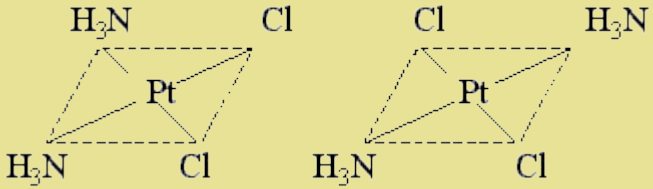
Pt metals are not essential for human body

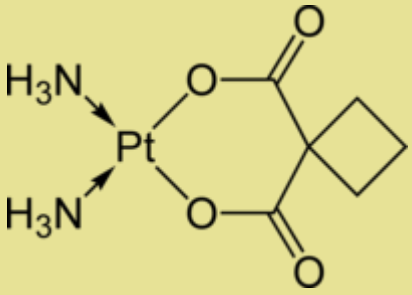
Their usage in medicine is limited.

OsO_4 **– is used in histology, but it is very toxic**

Pd **– is used is dentistry**

Cis-$[Pt(NH_3)_2Cl_2]$ **– cisplatin – is used to treat tumors (oncologic diseases) by the way of replication block caused by the formation of covalent bonds with guanines.**





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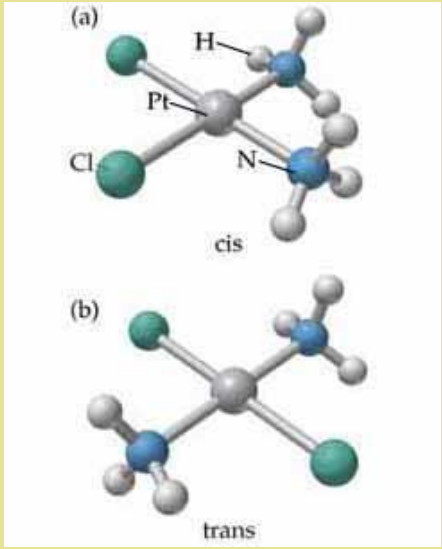
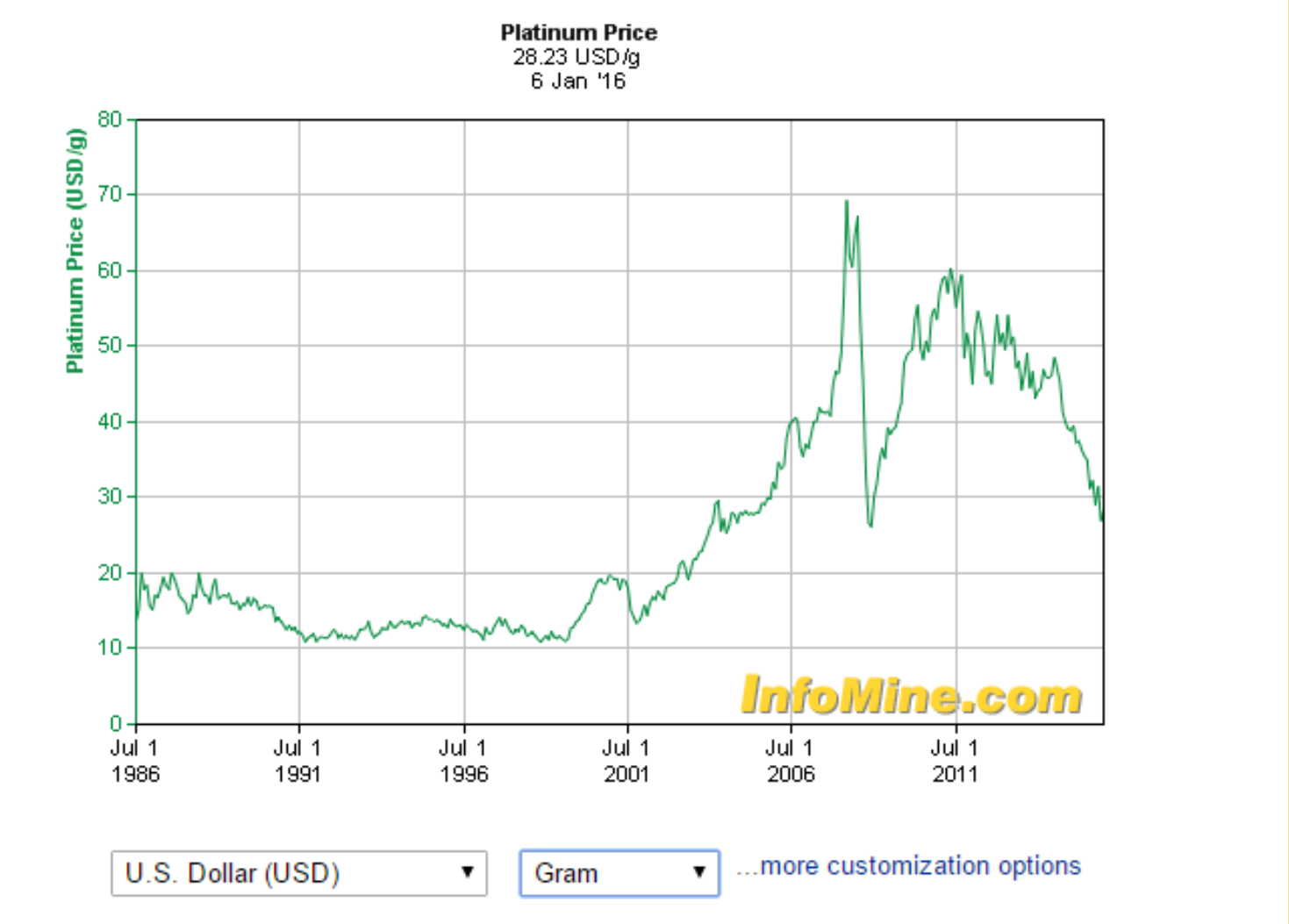


What's the price of gold?

What's the price of platinum?

What's the price of silver?



Thank you for listening!!!