



Inorganic Chemistry Department General and Inorganic Chemistry



Elements of VIIB, I-IB groups

In specialty 226 Pharmacy, industry pharmacy

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Plan of Lecture

- 1. Some properties of elements VIIIB group.**
- 2. Iron triad elements. Iron, Cobalt, Nickel compounds. Cations (II) and (III), its properties. Complex compounds of Iron Triad Elements.**
- 3. The Qualitative Reaction for Compounds Which Contain elements of Iron Triad.**
- 4. Biological role compounds of elements VIIIB group and their application in medicine.**
- 5. Some properties of elements I-IIB group.**
- 6. Compounds of Elements I-II groups in different oxidation states.**
- 7. The Qualitative Reaction for Compounds Which Contain elements of I-II B groups.**
- 8. Biological role compounds of elements I-IIB group and their application in medicine.**

Actuality of theme

Biologically active substances of elements of VIII B and I-IB groups are of great importance in pharmacy and medicine.

Aim: Depending on the electronic structure of elements of VIII B and I-IB groups, their properties and the place they occupy in medicine and pharmacy are determined.

Specific goals:

- Be able to write electronic formulas of elements of VIII B and I-IB groups in various degree of oxidation.
- Know the ways to get and use them in medicine.

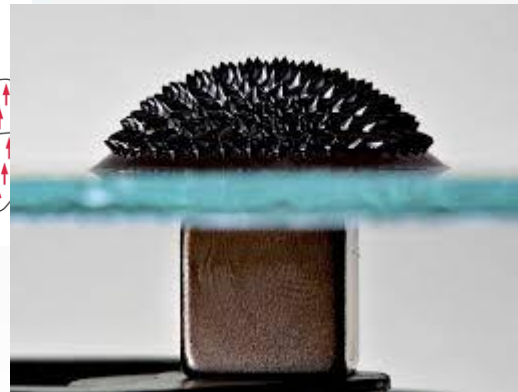
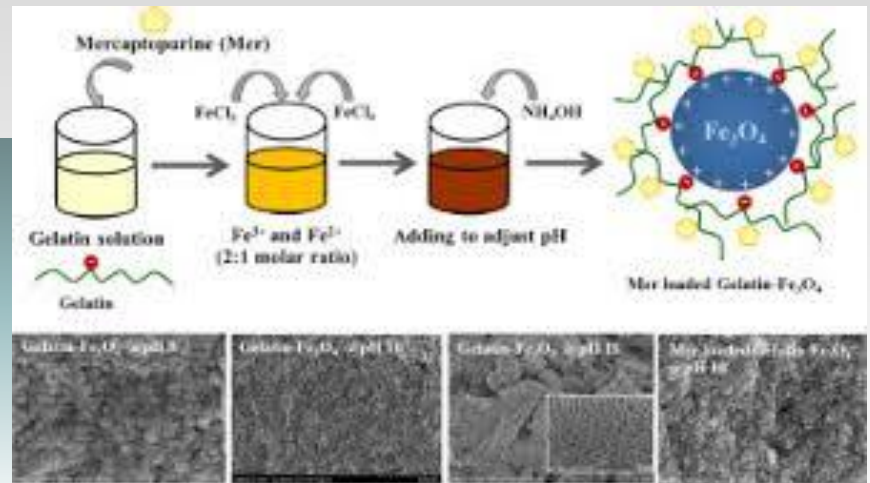
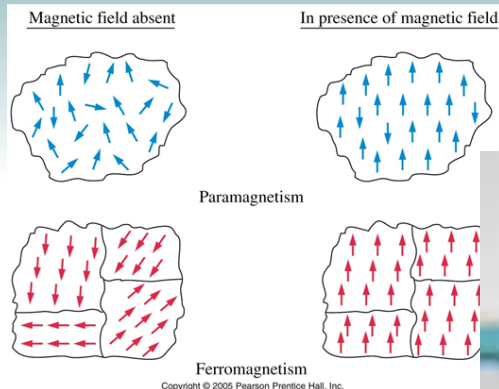
Theoretical questions for individual work

Iron Triad Elements. Properties of simple substances and their compounds.

Elements of I-IB. Properties of simple substances and their compounds.

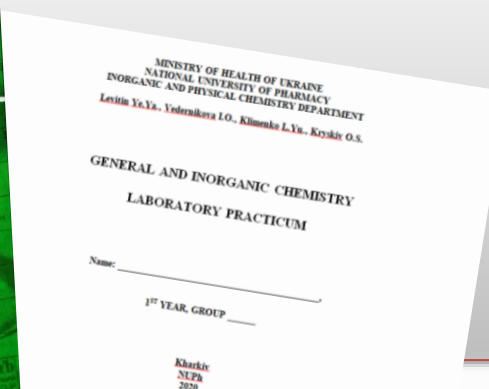
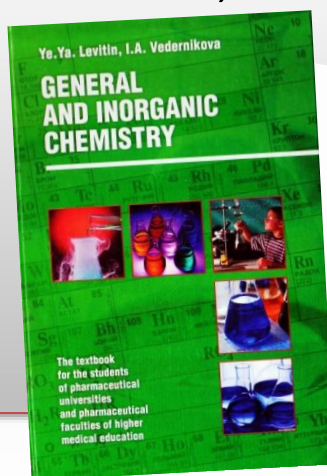
Ferromagnetism

- The iron triad exhibits **ferromagnetism** which is a much stronger magnetic effect than paramagnetism.
- A ferromagnetic solid consists of regions called *domains* in which atoms have their magnetic moments aligned.
- When placed in a magnetic field, all the domains are aligned and the solid becomes magnetized.



Bibliographical Guidance

- **General and inorganic chemistry: Textbook** for students of higher schools
Ye.Ya.Levitin, I.O.Vedernikova.– Kharkiv:Publishing House of NUPH :Golden Pages, 2009. – 360 p.
- **General and Inorganic Chemistry Laboratory Practicum** / Ye.Ya. Levitin, I.O. Vedernikova, L.Yu. Klimenko, O.S. Kryskiv. – Kharkiv, 2020. – 106 p.
- **General and inorganic chemistry: The lecture course** for the students of pharmaceutical universities and pharmaceutical faculties of higher medical education / Ye.Ya. Levitin, I.O. Vedernikova, L.Yu. Klimenko, O.S. Kryskiv. – Kharkiv: NUPH Publishers, 2020. – 123 p.
- **The collection of theoretical questions and tests** in inorganic chemistry:for the students of higher school. / Ye.Ya.Levitin, I.O.Vedernikova.– Kharkiv: NUPH Publishers, 2007. – 76 p.



The Elements of VIIB Group

1

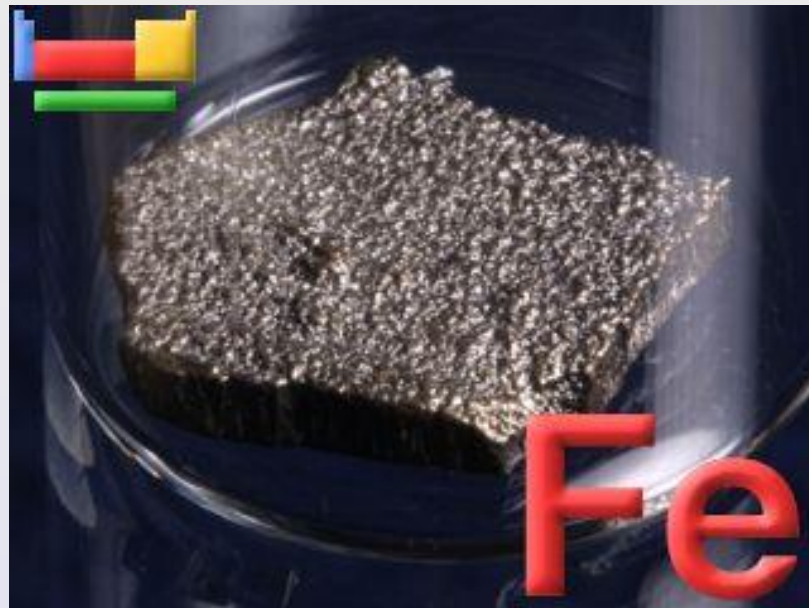
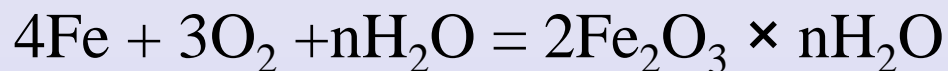
Iron	Fe^{26}	$[\text{Ar}] \underline{4s^2 3d^6}$
Cobalt	Co^{27}	$[\text{Ar}] \underline{4s^2 3d^7}$
Nickel	Ni^{28}	$[\text{Ar}] \underline{4s^2 3d^8}$

- d- sublevels are completed with valence electrons, these elements are the ***d-electronic families*** members

IRON

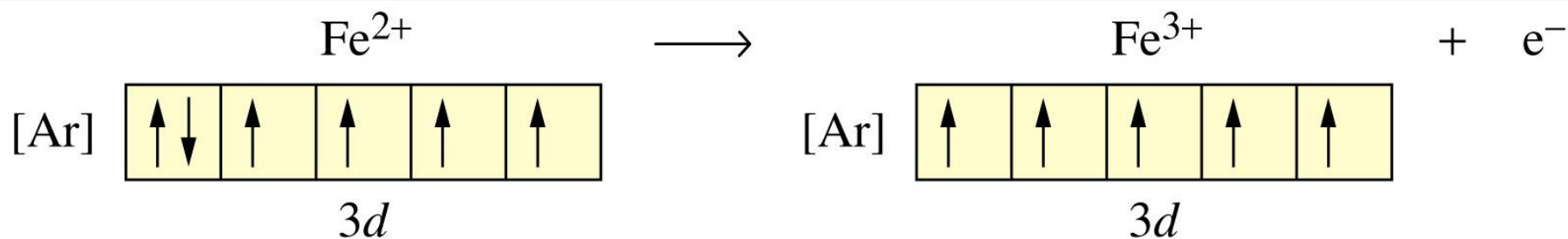
Brief description:

- Iron is a relatively abundant element in the universe.
- It is found in the sun and many types of stars in considerable quantity.
- Iron nuclei are very stable.
- Iron metal is a silvery, lustrous metal which has important magnetic properties.
- Iron is a vital constituent of plant and animal life, and is the key component of haemoglobin.
- The pure metal is not often encountered in commerce, but is usually alloyed with carbon or other metals.
- The pure metal is very reactive chemically, and rapidly corrodes, especially in moist air or at elevated temperatures.



The Iron Triad: Fe, Co, and Ni

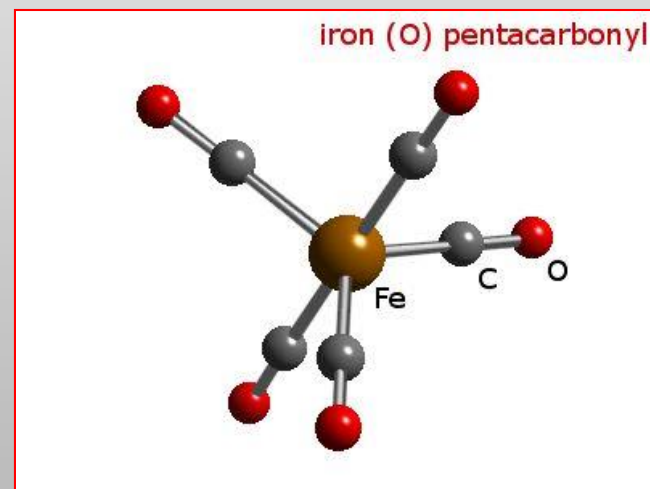
- Iron is the fourth most abundant element in Earth's crust. Cobalt and nickel are not nearly as common.
- All three elements form 2+ and 3+ ions.
- The most common ions of Co and of Ni are the 2+. The most common ion of Fe is the 3+ due to the half-filled *d*-subshell:





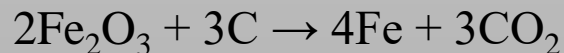
Isolation of iron:

The pure iron can be made through the purification of crude iron with carbon monoxide. The carbonyl decomposes on heating to about 250°C to form pure iron powder.



Nearly all iron produced commercially is used in the steel industry and made using a blast furnace.

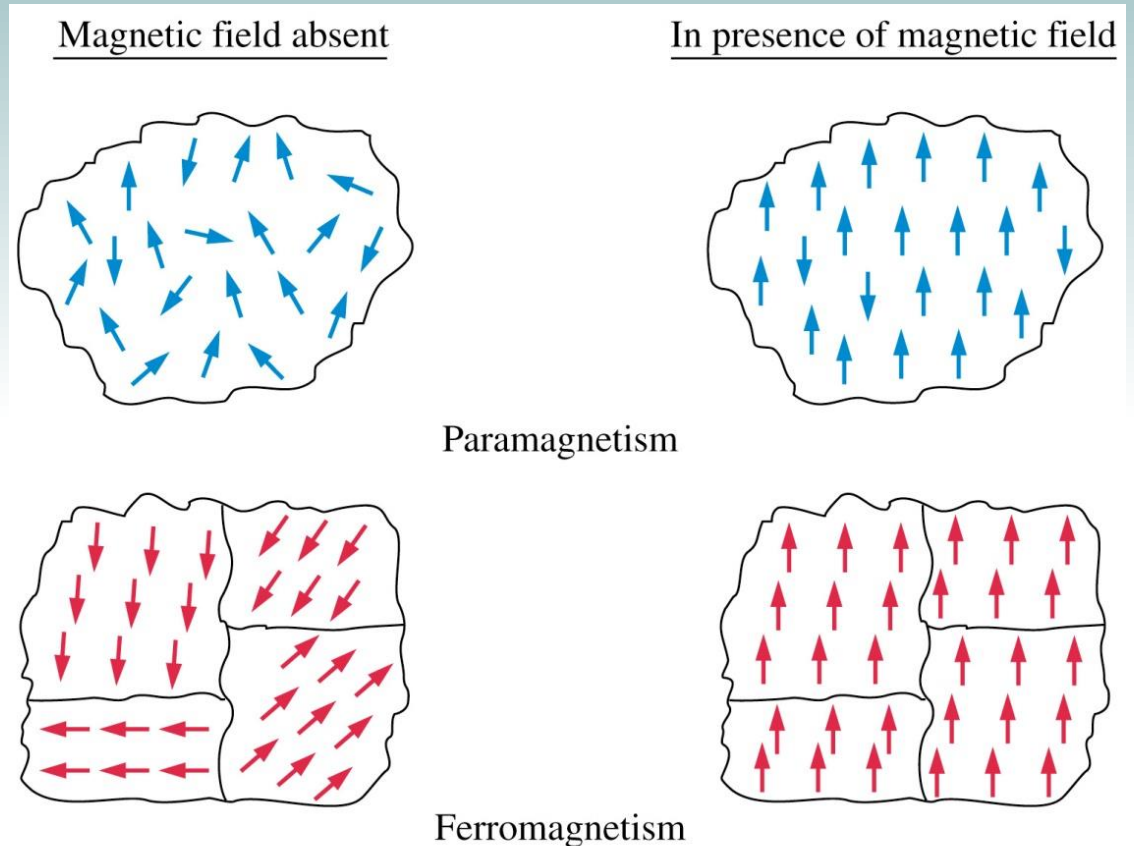
In this process iron oxide, is reduced with carbon (as coke):



This process is one of the most significant industrial processes in history and the origins of the modern process are traceable back to a small town called Coalbrookdale in Shropshire (England) around the year 1773.

Ferromagnetism

- The iron triad exhibits **ferromagnetism** which is a much stronger magnetic effect than paramagnetism.
- A ferromagnetic solid consists of regions called *domains* in which atoms have their magnetic moments aligned.
- When placed in a magnetic field, all the domains are aligned and the solid becomes magnetized.



Some compounds of elements

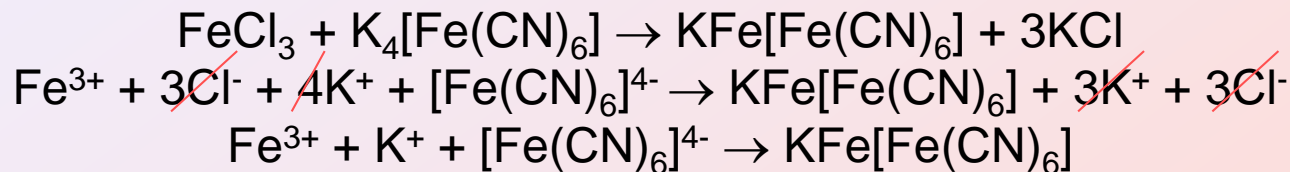
↑	oxidation state
—	+6 K_2FeO_4 potassium ferrate, $BaFeO_4$ barium ferrate
—	+3 Fe_2O_3 , $Fe(OH)_3$, $Fe(SCN)_3$, $K_3[Fe(CN)_6]$ potassium hexacyanoferrate (III) Co_2O_3 , $Co(OH)_3$, $[Co(NH_3)_6]Cl_3$ hexaamminecobalt (III) chloride Ni_2O_3 , $Ni(OH)_3$, $NiCl_3$ nickel (III) chloride
—	+2 FeO , $Fe(OH)_2$, $FeSO_4$, $K_4[Fe(CN)_6]$ potassium hexacyanoferrate (II) CoO , $Co(OH)_2$, $(CoOH)_2SO_4$ hydroxocobalt (II) sulfate NiO , $Ni(OH)_2$, $[NiCl_2(NH_3)_2]$ diamminedichloronickel
—	0 Fe, Co, Ni simple compounds,

Conclusion:

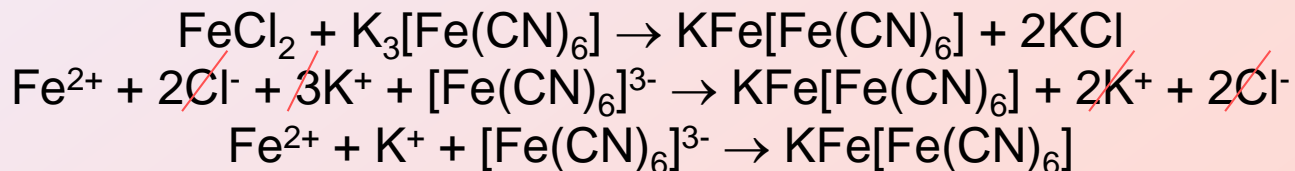
0, +2, +3 are the most typical oxidation state for iron, cobalt and nickel

The reactions of qualitative identification of iron compounds

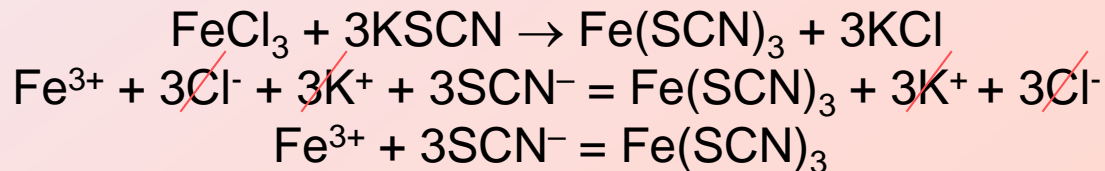
Iron (II) compounds yield a **blue precipitate**, Turnbull's blue, when treated with hexacyanoferrate (III) ion:



Iron (III) compounds yield a **blue precipitate**, Prussian blue, when treated with hexacyanoferrate (II) ion:

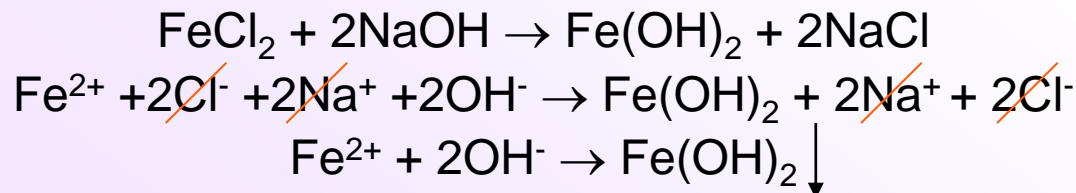


Iron (III) compounds yield a **dark red** coloration when treated with thiocyanate ion:



Iron (II) hydroxide

It produces white precipitate in the basic solution:

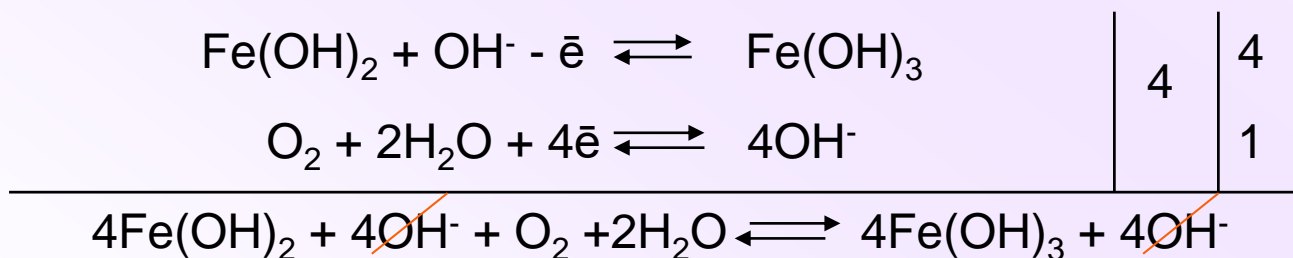


It is a weak electrolyte:

$$K_{\text{SP}} = [\text{Fe}^{2+}] \times [\text{OH}^-]^2 = 1 \times 10^{-15}$$

It reacts with acid: $\text{Fe(OH)}_2 + 2\text{HCl} \rightarrow \text{FeCl}_2 + 2\text{H}_2\text{O}$

It is easy oxidized: $\text{Fe(OH)}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3$

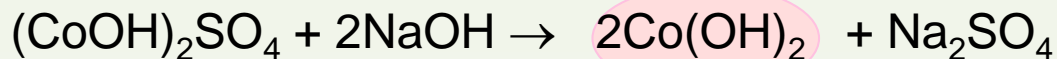
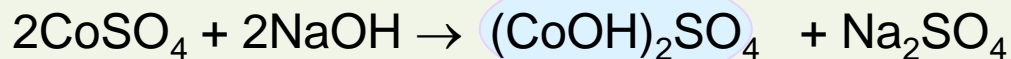


Conclusion:

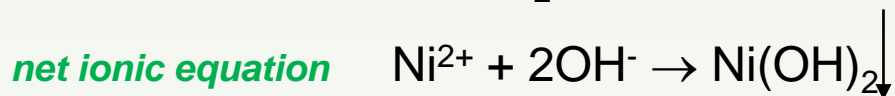
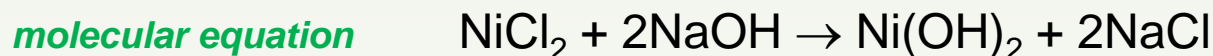
Iron (II) hydroxide is a weak electrolyte with basic properties.
It can be oxidized with oxygen of the air.

Cobalt (II) and nickel (II) hydroxides

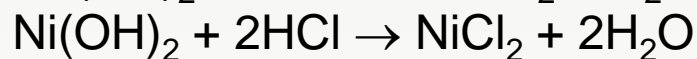
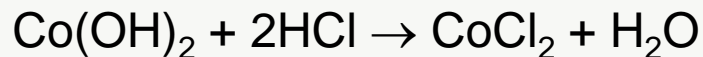
Cobalt (II) cation produces **blue precipitate** of basic salt at first, then **pink precipitate** in the excess of sodium hydroxide:



Nickel (II) hydroxide is produced in the basic solution:



Cobalt (II) and nickel (II) hydroxides react with acids:

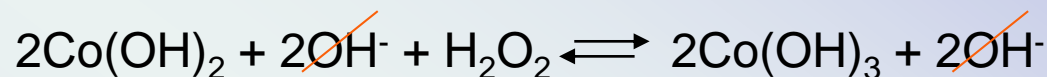
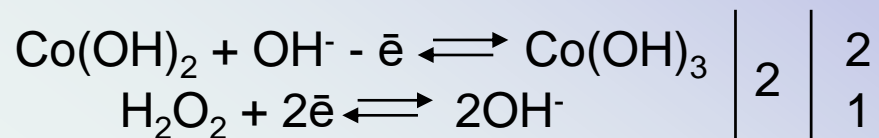
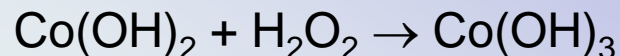


Conclusion:

Cobalt (II) and nickel (II) hydroxides are weak electrolytes with basic properties.

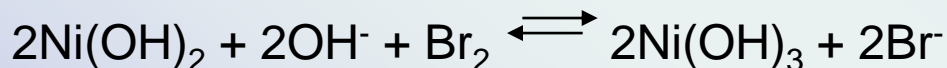
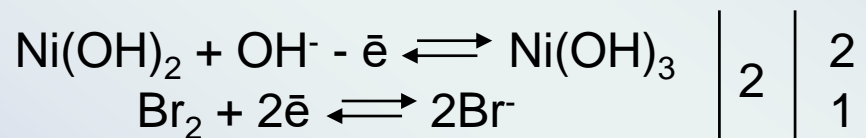
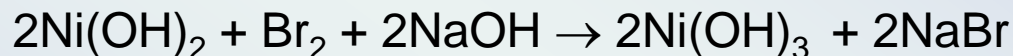
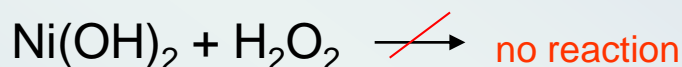
Reducing properties of hydroxides

Cobalt (II) hydroxide can be oxidized with hydrogen peroxide:



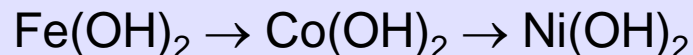
Nickel (II) hydroxide can be oxidized only

with strong oxidizing agent:



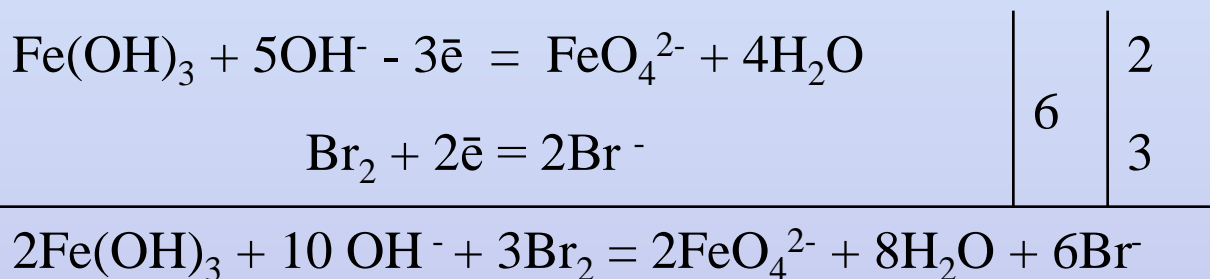
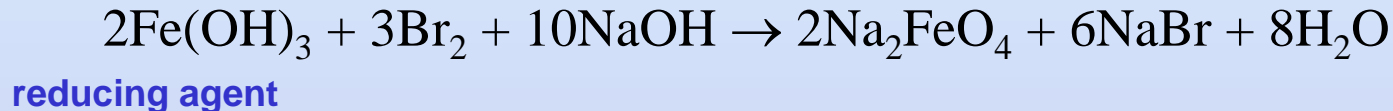
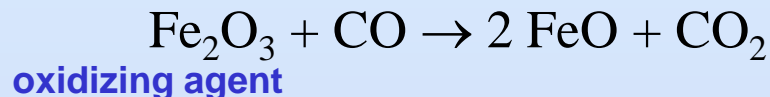
Conclusion:

The reducing properties of hydroxides are decreased:

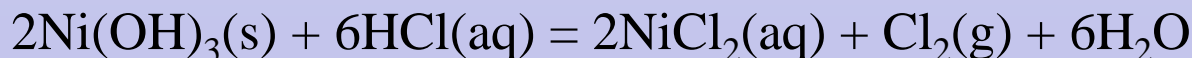
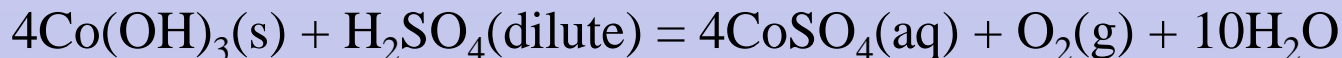


Compounds of Fe³⁺, Co³⁺ and Ni³⁺

Iron (III) cation can be reducing and oxidizing agent in ORR:



Co³⁺ and Ni³⁺ are very good **oxidizing agents**:

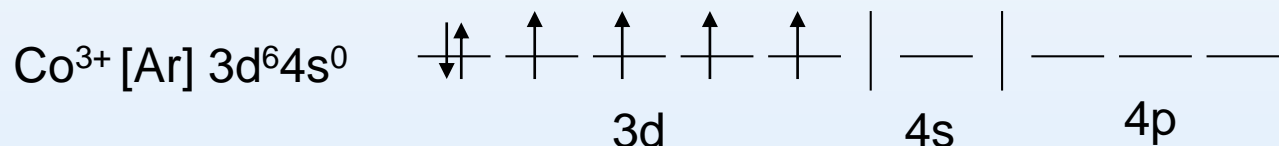
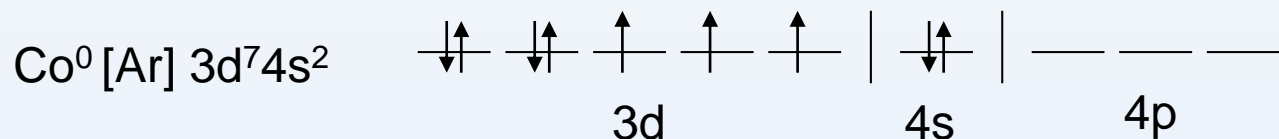


Complex compounds of cobalt (III)

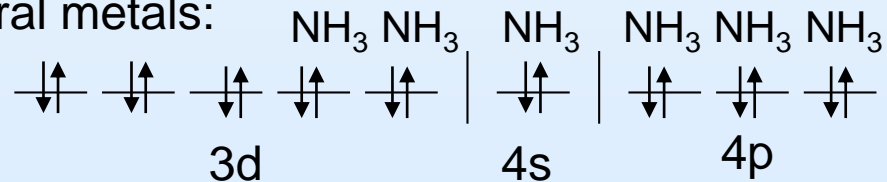
Hexaamminecobalt (III) ion is produced:



To explain the structure of complex ion use valence bond (VB) method:



Molecules NH_3 are ligands of average force and therefore couple electrons of the central metals:



Conclusion:

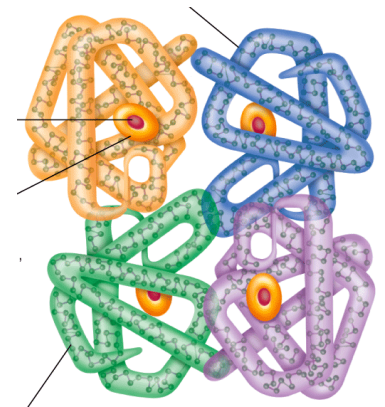
The central atom (Co^{3+}) has d^2sp^3 type of hybridization, The complex ion has octahedral structure, it is diamagnetic

Biological role of iron:

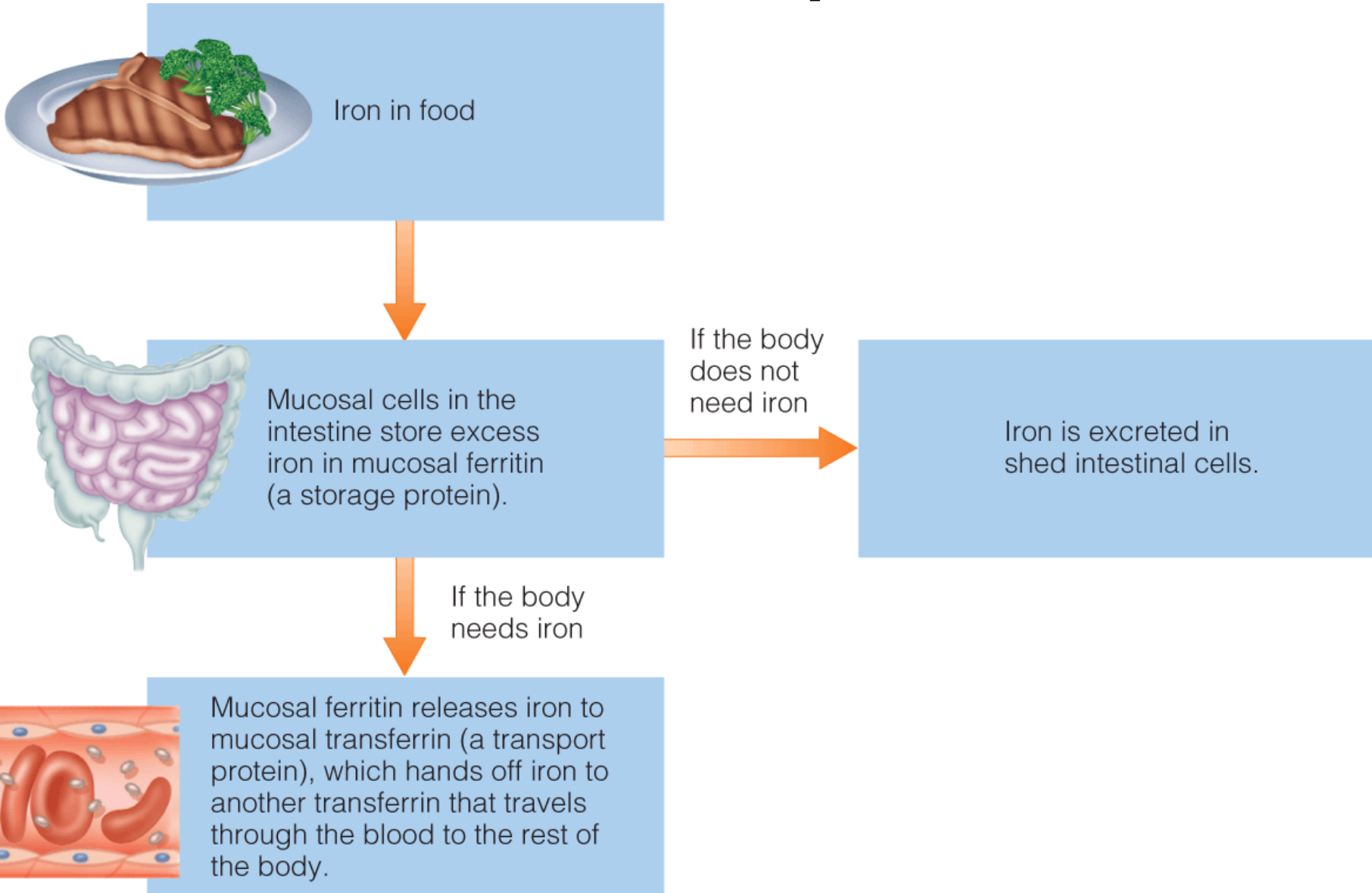
- Iron compounds are essential to all life.
- It is an iron atom in haemoglobin that is responsible for carrying oxygen around the blood stream.
- Iron deficiency leads to anemia.
- Excess iron in the body causes liver and kidney damage (haemochromatosis). Some iron compounds are suspected carcinogens.
- Good sources of dietary iron include red meat, fish, poultry, lentils, beans, leaf vegetables, tofu, chickpeas, black-eyed peas, fortified bread, and fortified breakfast cereals.
- Iron in low amounts is found in molasses and farina. Iron in meat (haem iron) is more easily absorbed than iron in vegetables, but heme/hemoglobin from red meat has effects which may increase the likelihood of colorectal cancer.

Iron: Functions

- Part of the protein hemoglobin, which carries oxygen in the blood
- Part of the protein myoglobin in muscles, which makes oxygen available for muscle contraction
- Necessary for the utilization of energy as part of the cells' metabolic machinery



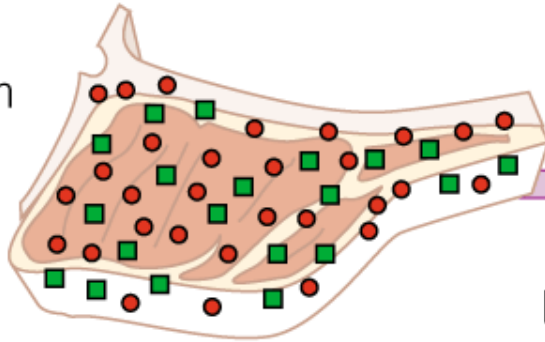
Iron Absorption



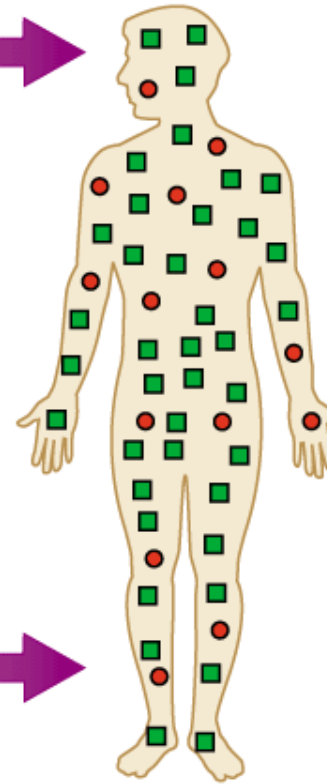
Iron: Heme vs. Nonheme

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Only foods derived from animal flesh provide heme, but they also contain nonheme iron.



Heme accounts for about 10% of the average daily iron intake, but it is well absorbed (about 25%). Nonheme iron accounts for the remaining 90% but it is less well absorbed (about 17%).



Key:

- Heme
- Nonheme

All the iron in foods derived from plants is nonheme iron.



Iron Fe (Ferrum)

important microelement human body: 4–5 g Fe

a) functional form - heme iron proteins

hemoglobin 70 %

myoglobin 5 %

some enzymes - non-heme iron proteins

b) transport form (transferrin)

c) storage of iron (ferritin, hemosiderin)-20 %

Fe in food 10-30 mg/day

absorption: only 7-10% → ~ 1 mg/day

HEME iron proteins

Hemoglobin - O₂ transport in blood

- in red blood cells

- *tetramer = 4 subunits*

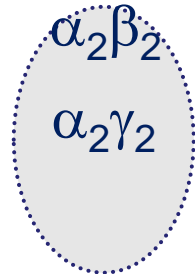
each subunit: one heme + one globin

HbA ("adult")

$\alpha_2\beta_2$

HbF ("fetal")

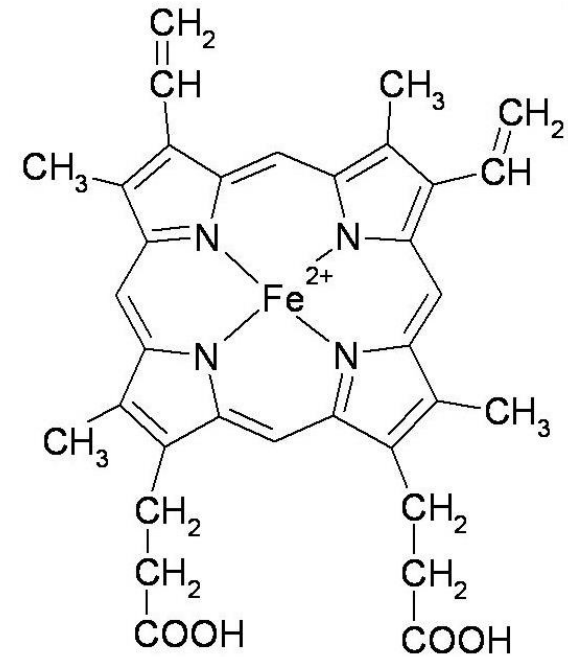
$\alpha_2\gamma_2$



Myoglobin - "O₂ storage" in muscle cell

Cytochromes - electron transport

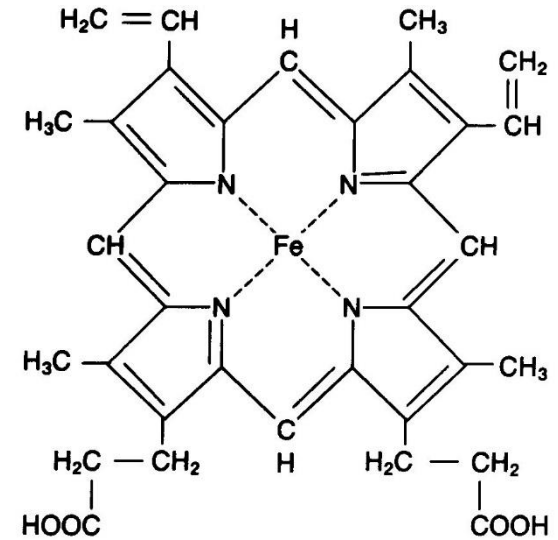
- their function is based on: Fe^{2+} (reduced) \rightleftharpoons Fe^{3+} (oxidized)



heme

Iron forms in diets

- Heme
 - Iron-porphyrin prosthetic group
 - Hemoglobin, myoglobin, cytochromes
 - Other iron-containing enzymes are ~3% body iron
 - Aconitase, peroxidases
 - 5-25% are absorbed
 - Exist as Fe^{2+}



- Nonheme
 - >85% of iron in foods is non heme iron
 - 2-5% are absorbed
 - Exist as Fe^{3+}

Storage Status

- Iron Deficiency
 - Subtle symptoms unless anemia is severe (hemoglobin <70g/L)
 - Mainly three identified (from least to most severe)
 - ◆ Storage iron depletion
 - Only iron store is depleted
 - ◆ Early functional iron deficiency
 - Iron store is depleted and functional iron is low but not low enough to cause measurable anemia
 - ◆ Iron deficiency anemia
 - Impaired tissue oxygenation, reduced work ability
 - Responsible for many maternal death at parturition
 - Impaired oxidative metabolism in muscle
 - shift to gluconeogenesis and lactate utilization (acidosis)
 - Behavioral and Intellectual Defects
 - Body temperature regulation impaired

Deficiency Signs



**Koilonychia
"Spoon Nails"**

Glossitis



Angular Stomatitis



Storage Status

- Iron Excess & Toxicity
 - Acute toxicity - overload transferrin, strong acids produced by Fe/HCl in stomach kill GI tract
 - Bloody vomit and stools
 - Systemic effects from conversion of ferrous to ferric and release of protons

Storage Status

- Iron Excess & Toxicity

- Chronic Iron Toxicity

- Hemosiderosis - excess iron in hemosiderin
 - Hemochromatosis - excess iron in fibrotic tissue damage
 - common causes = excess ingestion or transfusion
 - Genetic hyper absorption - Hemochromatosis
 - » 3-4/100 of European descent
 - » Cirrhosis, diabetes, heart failure, arthritis, sexual dysfunction
 - » *Transferrin saturation good screening test*

The Elements of IB Group

1

<i>Copper</i>	Cu^{29}	$[\text{Ar}] \underline{3d^{10} 4s^1}$
<i>Silver</i>	Ag^{47}	$[\text{Kr}] \underline{4d^{10} 5s^1}$
<i>Gold</i>	Au^{79}	$[\text{Xe}] 4f^{14} \underline{5d^{10} 6s^1}$

The Elements of IIB Group

<i>Zinc</i>	Zn^{30}	$[\text{Ar}] \underline{3d^{10} 4s^2}$
<i>Cadmium</i>	Cd^{48}	$[\text{Kr}] \underline{4d^{10} 5s^2}$
<i>Mercury</i>	Hg^{80}	$[\text{Xe}] 4f^{14} \underline{5d^{10} 6s^2}$

Some compounds of elements

↑ <i>oxidation state</i>	
+3	Au ₂ O ₃ aurum (III) oxide, H[AuCl ₄] hydrogen tetrachloroaurumate (III)
+2	ZnO zinc oxide, CdO cadmium oxide, HgO mercury (II) oxide CuO copper (II) oxide, Cu(OH) ₂ copper (II) hydroxide, CuSO ₄ copper (II) sulfate, (CuOH) ₂ CO ₃ hydroxocopper (II) carbonate
+1	Ag ₂ O silver oxide, Cu ₂ O copper oxide Au ₂ O aurum (I) oxide, K[Au(CN) ₂] potassium dicyanoaurumate (I) Hg ₂ O mercury (I) oxide, Hg ₂ Cl ₂ mercury (I) chloride, Hg ₂ (NO ₃) ₂ mercury (I) nitrate
0	Cu, Ag, Au simple compounds, Zn, Cd, Hg simple compounds

Conclusion: 0, +3 are the most typical oxidation states for **gold**
 0, +1, +2 are the most typical oxidation states for **copper** and **mercury**
 0, +2 are the most typical oxidation states for **zinc** and **cadmium**
 0, +1 are the most typical oxidation states for **silver**

The elements of IB group

Copper is used extensively in electrical wiring and circuitry. Gold contacts are sometimes found in precision equipment for their ability to remain corrosion-free. Silver is used widely in mission-critical applications as electrical contacts, and is also used in photography (because silver nitrate reverts to metal on exposure to light), agriculture, medicine, audiophile and scientific applications.



The elements of IIB group

Cadmium is a soft, bluish-white metal and is easily cut with a knife. It is similar in many respects to zinc. Cadmium and its compounds are highly toxic. Silver solder, which contains cadmium, should be handled with care.

Cadmium burns in air to form brown amorphous cadmium oxide:
$$\text{Cd} + \text{O}_2 \rightarrow \text{CdO}$$

Hydrochloric acid, sulfuric acid and nitric acid dissolve cadmium by forming cadmium chloride (CdCl_2) cadmium sulfate (CdSO_4) or cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$).



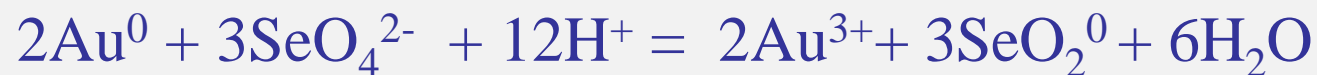
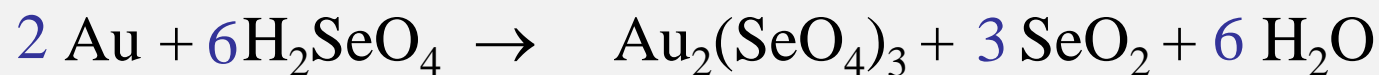
Mercury is the only common metal liquid at ordinary temperatures. Mercury is sometimes called quicksilver. It rarely occurs free in nature and is found mainly in cinnabar ore (HgS) in Spain and Italy. It is a heavy, silvery-white liquid metal. It alloys easily with many metals, such as gold, silver, and tin. These alloys are called amalgams.

Dissolution of gold

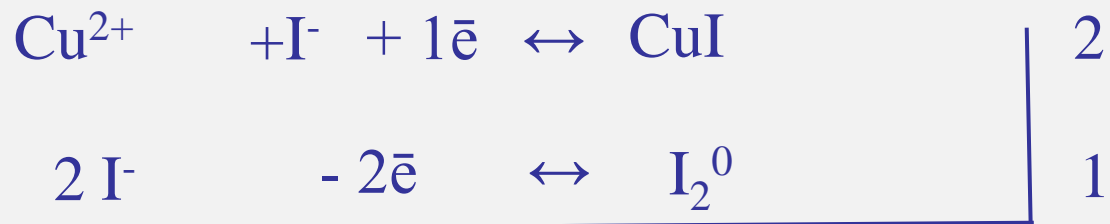
1) In the «aqua regia»:



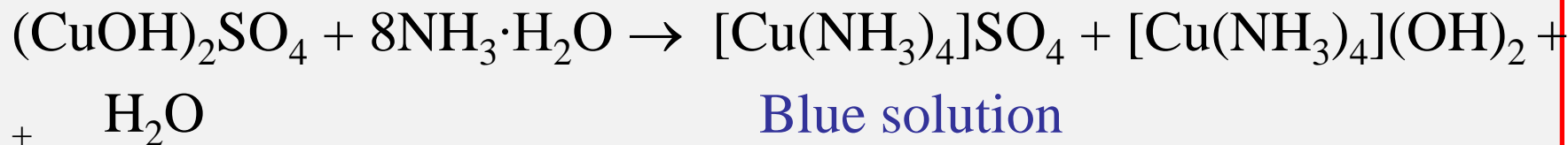
2) In the selenium acid at heating:



Oxidizing properties of copper(II)

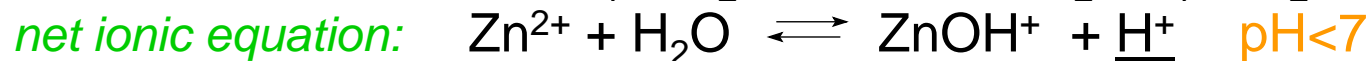
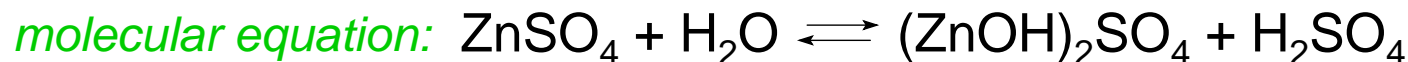


The reaction of qualitative identification of copper (II)



The hydrolysis of zinc (II)

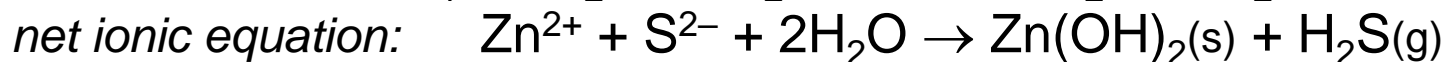
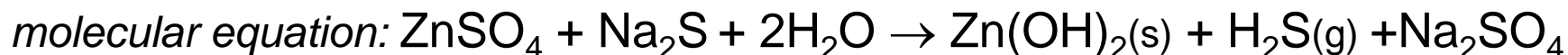
The salts of zinc (II) undergoing hydrolysis. Under normal condition they hydrolyse only at the first step



Conclusion:

Due to hydrolysis the solutions of zinc (II) salts have acidic medium
Indicator **methyl-orange** into these solution has **pink color**

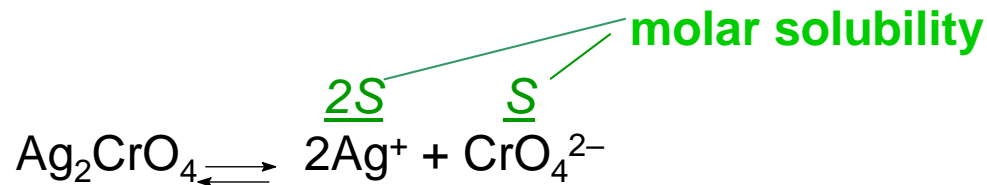
Irreversible hydrolysis (co-hydrolysis):



Conclusion:

If salt is formed by the weak, insoluble basis and weak acid, unstable in a solution, the hydrolysis reaction proceeds up to the end (such salts do not exist in a solution and may be received only by thermal interaction of simple substances).

Some compounds of silver are insoluble



The value of the *solubility product constant* of silver (I) chromate:

$$K_{\text{sp}} = 2.4 \times 10^{-12}$$

The expression of the *solubility product constant* of silver (I) chromate:

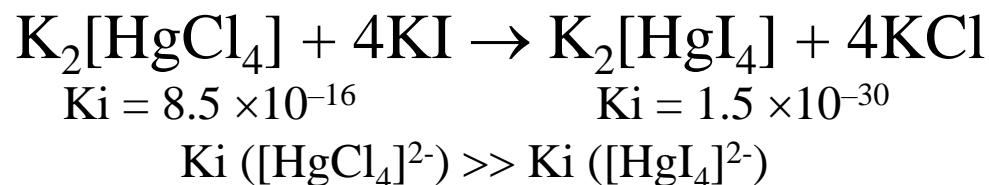
$$K_{\text{sp}} = [\text{Ag}^+]^2 \times [\text{CrO}_4^{2-}] = (2S)^2 \times S = 4S^3$$

$$4S^3 = 2.4 \times 10^{-12} \text{ (mol} \times \text{L}^{-1}\text{)}; \quad S = 8.43 \times 10^{-5} \text{ (mol} \times \text{L}^{-1}\text{)}$$

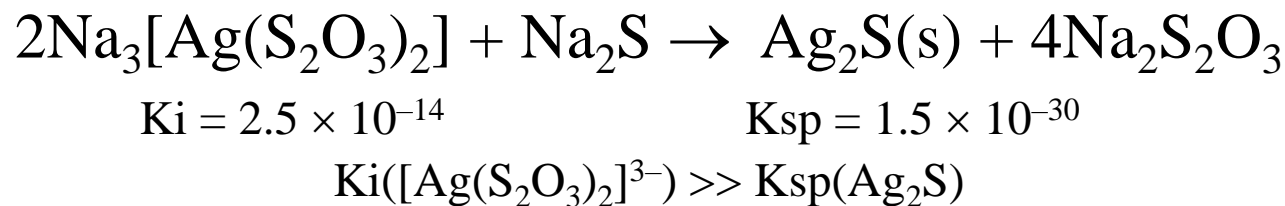
$$S(\text{g} \times \text{L}^{-1}) = S(\text{mol} \times \text{L}^{-1}) \times M(\text{Ag}_2\text{CrO}_4) = 331.6 \times 8.43 \times 10^{-5} = 2.79 \times 10^{-2} (\text{g} \times \text{L}^{-1})$$

Using values of K_i or the value K_{sp} , it is possible to predict a direction of reactions

At addition of solution KI to a solution $K_2[HgCl_4]$ is formed new stronger complex $K_2[HgI_4]$ which constant of instability is much less, than the constant of initial complex:



At addition Na_2S to solution $Na_3[Ag(S_2O_3)_2]$ the slightly soluble in water Ag_2S is formed:

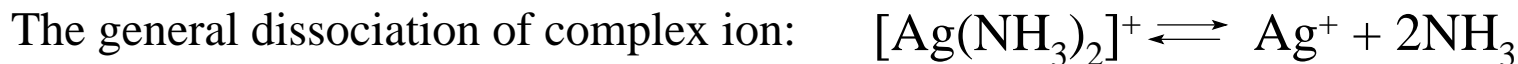


Electrolytic Dissociation of Complex Ions in Solutions

Initial dissociation – disintegration of coordination compounds on a complex ion and ions of external sphere. It is irreversible:



Secondary dissociation of complex ion. It is reversible:

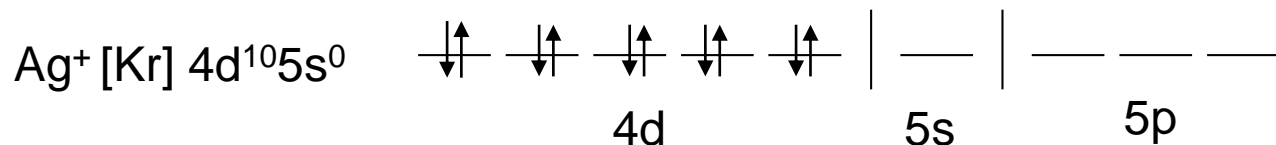
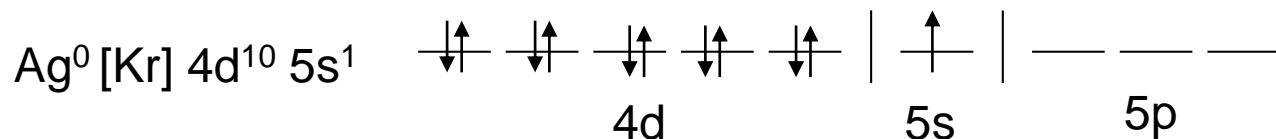
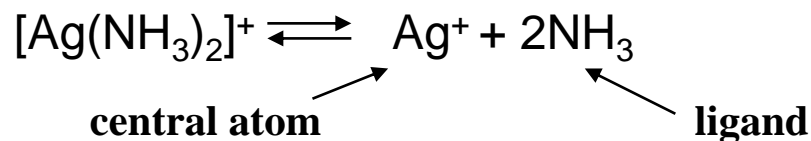


The expression of general **instability constant**:

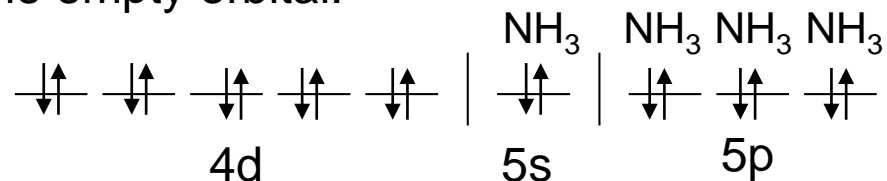
$$K_{i_{gen.}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[[\text{Ag}(\text{NH}_3)_2]^+]}$$

The Structure of Complex Compounds

To explain the structure of complex ion use valence bond (VB) method:



The electrons of ligands NH_3 occupy the empty orbital:



Conclusion:

The central atom Ag^+ has sp^3 type of hybridization,
The complex ion has tetrahedral structure, it is diamagnetic.

CONCLUSION:

Biological role of IB elements

Copper is found widely in tissues, with concentration in liver, muscle, and bone. It functions as a co-factor in various enzymes and in copper-based pigments. The RDA for copper in normal healthy adults is 0.9 mg/day. An inherited condition called Wilson's disease causes the body to retain copper, since it is not excreted by the liver into the bile. This disease, if untreated, can lead to brain and liver damage.



Silver compounds are sold as remedies for a wide variety of diseases. Silver has wide-spectrum of antimicrobial activity. Colloidal silver preparations are harmless, some people using these home-made solutions excessively have developed argyria over a period of months or years. High doses of colloidal silver can result in coma, pleural edema, and hemolysis.

Some gold salts do have anti-inflammatory properties and are used as pharmaceuticals in the treatment of arthritis and other similar conditions. Gold alloys are used in restorative dentistry, especially in tooth restorations, such as crowns and permanent bridges. Colloidal gold is used in research applications in medicine, biology and materials science. The isotope gold-198, (half-life: 2.7 days) is used in some cancer treatments and for treating other diseases.

Biological role of IIB elements

Zinc is included in most single tablet over-the-counter daily vitamin and mineral supplements. Zinc gluconate is one compound used for the delivery of zinc as a dietary supplement. Zinc is found in nearly 100 specific enzymes, serves as structural ions in transcription factors and is stored and transferred in metallothioneins. Zinc has antioxidant properties, which protect against premature aging of the skin and muscles of the body. Zinc gluconate glycine and zinc acetate are used in throat lozenges or tablets to reduce the duration and the severity of cold symptoms. Zinc preparations (zinc oxide, zinc acetate and zinc gluconate) can protect against sunburn in the summer and windburn in the winter. Zinc lactate is used in toothpaste to prevent halitosis. Zinc pyrithione is widely applied in shampoos because of its anti-dandruff function. Zinc ions are effective antimicrobial agents even at low concentrations.

Cadmium is toxic but one enzyme (carbonic anhydrase) with a cadmium as reactive centre has been discovered.

Mercury and most of its compounds are extremely toxic and are generally handled with care. Mercury and its compounds have been used in medicine, although they are much less common today than they once were, now that the toxic effects of mercury and its compounds are more widely understood. Mercury compounds are found in some over-the-counter drugs, including topical antiseptics, stimulant laxatives, diaper-rash ointment, eye drops, and nasal sprays. Mercury is still used in some diuretics, although substitutes now exist for most therapeutic uses.

*Thank you
for
attention!*