Lecture №5

Chemical properties of elements from VIIIB subgroup

The plan of the lecture

1.Overall characteristic of elements from VIIIB subgroup

2.Natural resources

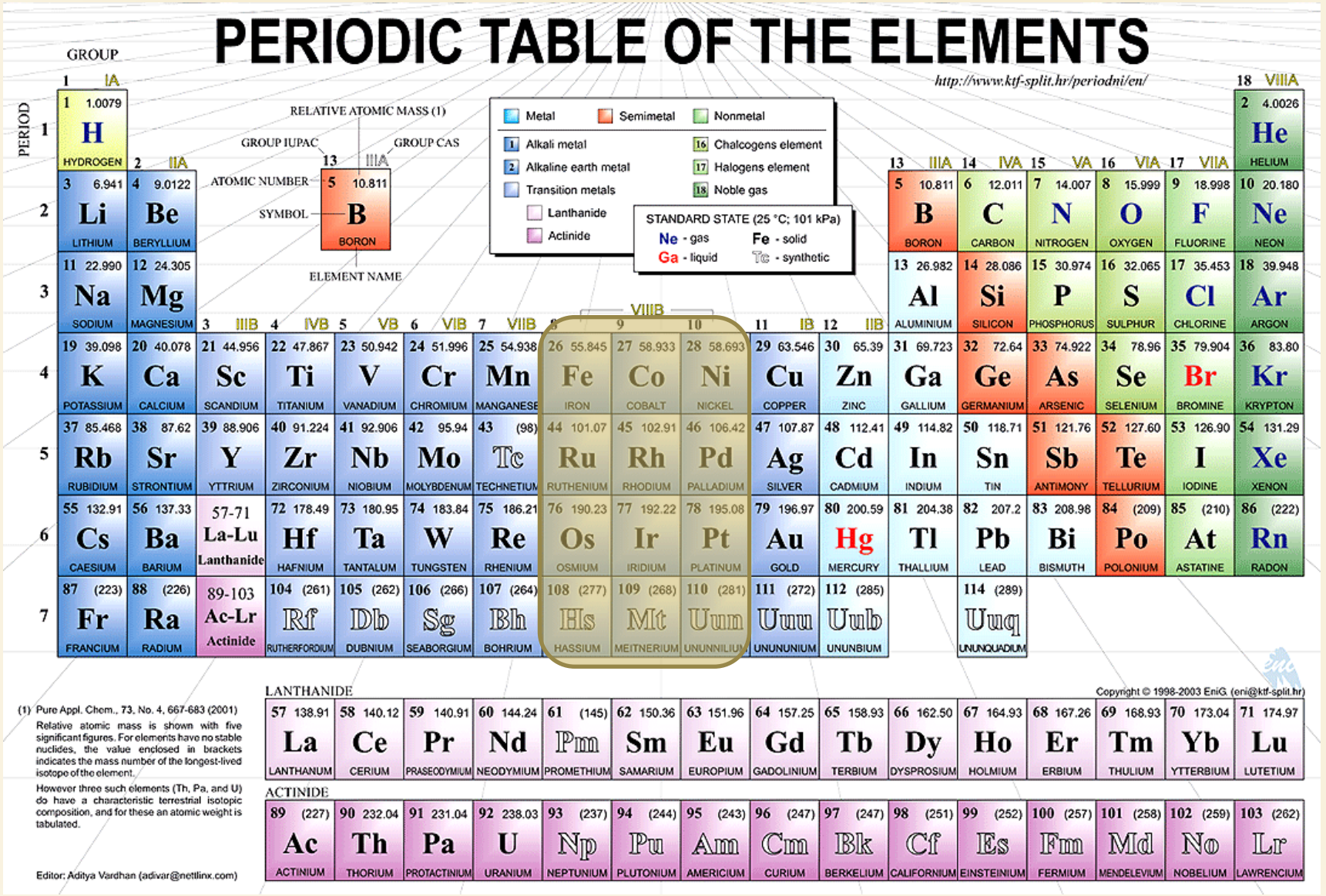
3.Physical and chemical properties of elements from the iron family

4.Main compounds of elements from iron family

5.Iron containing medicines

6.Iron containing substances in pharmaceutical analysis

7. The usage of cobalt and nickel in medicine and pharmacy


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
Fe - solid
Ga - liquid
Tc - synthetic
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 VIIIB
9 VIIIB
10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
1 1.0079 H HYDROGEN
2 4.0026 He HELIUM
3 6.941 Li LITHIUM
4 9.0122 Be BERYLLIUM
5 10.811 B BORON
6 12.011 C CARBON
7 14.007 N NITROGEN
8 15.999 O OXYGEN
9 18.998 F FLUORINE
10 20.180 Ne NEON
11 22.990 Na SODIUM
12 24.305 Mg MAGNESIUM
13 26.982 Al ALUMINIUM
14 28.086 Si SILICON
15 30.974 P PHOSPHORUS
16 32.065 S SULPHUR
17 35.453 Cl CHLORINE
18 39.948 Ar ARGON
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
37 85.468 Rb RUBIDIUM
38 87.62 Sr STRONTIUM
39 88.906 Y YTTRIUM
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
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
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) Uun UNUNNILIUM
111 (272) Uuu UNUNUNIUM
112 (285) Uub UNUNBIUM
114 (289) Uuq UNUNQUADIUM
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 YTTERBIUM
71 174.97 Lu LUTETIUM
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
(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.
Editor: Aditya Vardhan (adivar@netlinx.com)
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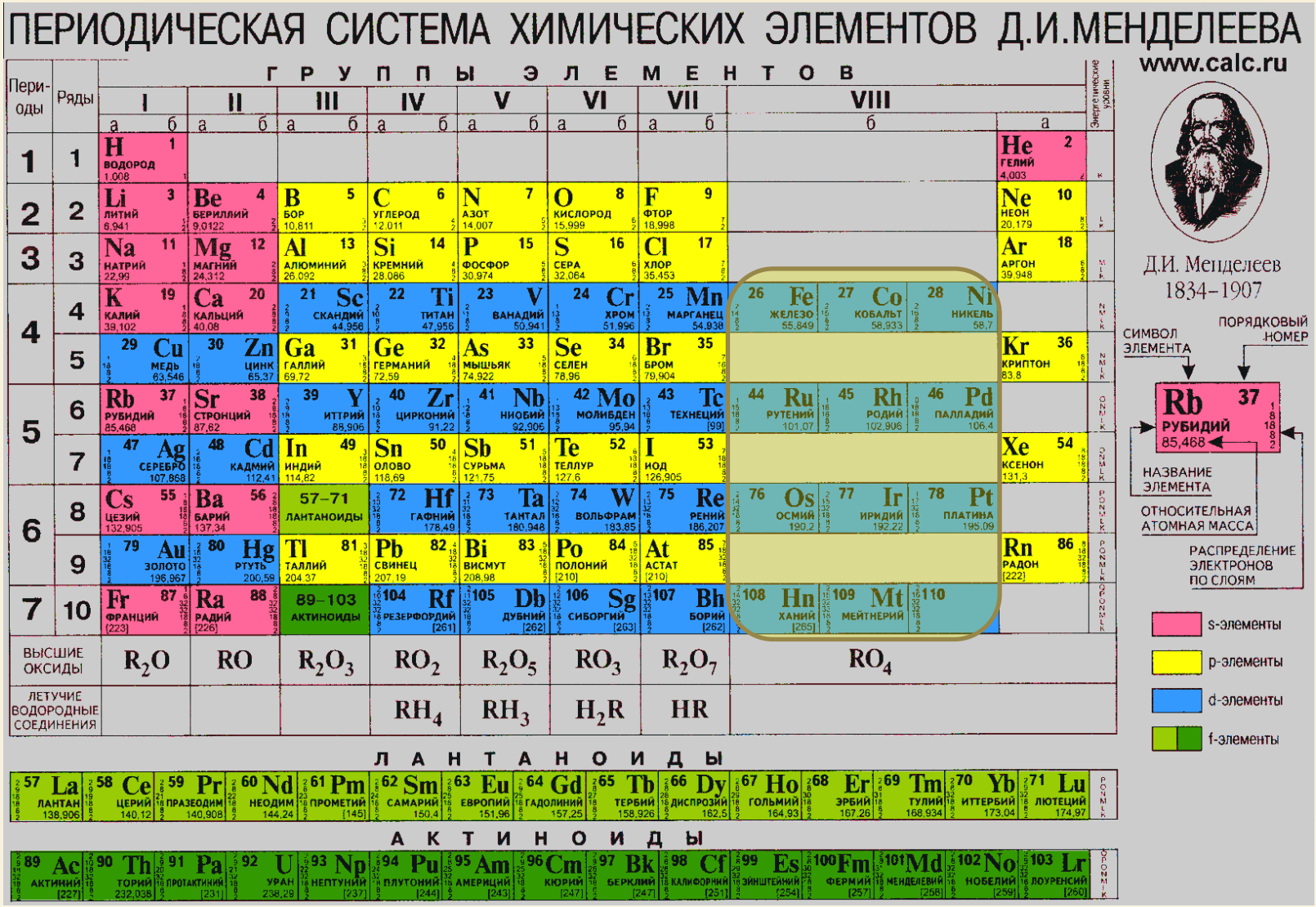
Old version of the table



1.Overall characteristic of d-elements from VIIIB subgroup

Properties of Fe, Co and Ni are very similar, but they are different from properties of VIIIB subgroup elements from 5^{th} and 6^{th} periods.

Because of this reason Fe, Co and Ni are usually described together as the elements from the "iron family", while heavy metals from VIIIB subgroup (Ru, Rh, Pd, Os, Ir, Pt) are described as the elements from the "platinum family".

2. Natural resources of VIIIB subgroup elements

Iron is the most abundant metal in the Earth crust after aluminum. As a pure chemical elements it can be found in meteorites (~ 300 ton of them fall on the Earth each year).

Minerals with Fe

FeS_2 – pyrite (iron persulfide; fool's gold)

$FeCO_3$ – syderite

Fe_2O_3 – hematite

$FeO(OH)$ – ironstone

Fe_3O_4 $(FeO \cdot Fe_2O_3)$ – magnetite

Cobalt **– can be found in cobaltine (CoAsS), as well as in polymetalic ores, nickel can be found in mixed sulfide minerals like $(Fe, Ni)_9S_8$**

Elements from platinum family are very rare. They exist mostly as pure elements. However, natural platinum contains about ≈ 80% of Pt itself, 10% of other metals like Fe, Au, Cu, and other impurities.

3. Physical and chemical properties of metals from iron family

Iron is white-gray (Fe), cobalt is pink-gray (Co), nickel is yellow-gray (Ni). Pure metals are durable and plastic, they have high melting points. Metals from the iron family are ferromagnetic.

In the absence of water iron is resistant to O_2, S, Cl_2, Br_2. At higher temperature those elements react with almost all nonmetals.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

$$3Fe + 2O_2 \rightarrow Fe_3O_4 \quad (t = 570°C)$$

$$2Fe + O_2 \rightarrow 2FeO \quad (t = 1200 – 1300°C)$$

Dispersed iron, nickel and cobalt spontaneously burn at normal temperature

Fe, Co and Ni react with carbon and form carbides of a variable content, but more often Me_3C.

Hydrogen can be dissolved in Fe, Co, Ni.

Nitrogen at high concentration can react with iron and form Fe_2N; Co and Ni cannot react with nitrogen.

These metals form sulfides with sulfur at high temperature.

Binary compounds of iron and sulfur are usually nonstoichiometric: FeS_x ($1 \leq x \leq 1.4$).

Reaction of iron and chlorine gas

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

Ions of metals can be hydrated or anhydrous

$[Me(H_2O)_6]^{2+}$

Fe^{2+} – pale-green

Co^{2+} – bright-violet

Ni^{2+} – bright-green

$CoCl_2 \cdot 6H_2O$

$NiCl_2 \cdot 6H_2O$

$CoCl_2$ anhydrous

$NiCl_2$ anhydrous

Interactions of iron and water

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2\uparrow$ (t = 570°C)

$Fe + H_2O \rightarrow FeO + H_2\uparrow$ (t = 900°C)

$Fe + H_2O \neq$ (t = 25°C)

$4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3\downarrow$ (t = 25°C)

Metals are passivated by concentrated H_2SO_4 and HNO_3 in the cold.

$$Fe + 6HNO_3(conc.) \xrightarrow{t} Fe(NO_3)_3 + 3NO_2 + 3H_2O$$

$$3Co + 8HNO_3(dilute) \xrightarrow{t} 3Co(NO_3)_2 + 2NO + 4H_2O$$

$$3Ni + 8HNO_3(dilute) \xrightarrow{t} 3Ni(NO_3)_2 + 2NO + 4H_2O$$

$$2Fe + 6H_2SO_4(conc.) \xrightarrow{t} Fe_2(SO_4)_3 + 3SO_2 + 6H_2O$$

Just iron (from the iron family) reacts with a hot solution of alkali.

$$Fe + 4NaOH(conc.) + 2H_2O \xrightarrow{t} Na_4[Fe(OH)_6] + H_2$$

The most studied compounds of elements from the iron family

COMPOUNDS WITH METALS IN +2 OXIDATION STATE

a) oxides MeO

FeO – black

CoO – gray-green

NiO – green

they cannot be dissolved in H_2O, but they are rather basic than acidic

$$MeO + 2HCl \rightarrow MeCl_2 + H_2O$$

CoO can be dissolved only in boiling concentrated solutions of alkali

$$CoO + 2NaOH + H_2O \rightarrow Na_2[Co(OH)_4]$$

FeO reacts with NaOH during the melting process:

$$FeO + 4NaOH \rightarrow 2H_2O + Na_4FeO_3$$

б) hydroxides $Me(OH)_2$ $\rightarrow$ $Me^{2+} + 2OH^- \rightarrow Me(OH)_2\downarrow$

$Fe(OH)_2$ – colorless

$Co(OH)_2$ – pink

$Ni(OH)_2$ – green

$Co^{2+} + OH^- \rightarrow CoOH^+$ *(blue)*

$CoOH^+ + OH^- \rightarrow Co(OH)_2$ *(pink)*

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ $Fe(OH)_2$ *is oxidized to*

$4Fe(OH)_2 + O_2 \rightarrow 4FeO(OH) + 2H_2O$ *iron (III) metahydroxide*

Hydroxides of $Me(OH)_3$ formula are not known, while $Fe(OH)_3$ is widely used in the chemistry course as an approximate formula for:

$Fe_2O_3 \cdot nH_2O \approx Fe(OH)_3$

$Ni(OH)_2$ cannot react with O_2. $Co(OH)_2$ reacts with O_2 slowly. These hydroxides react with acids. Acidic properties of $Me(OH)_2$ hydroxides are very weak.

$2NaOH + Fe(OH)_2 \rightarrow Na_2[Fe(OH)_4]$ *gray-green*

$2NaOH + Co(OH)_2 \rightarrow Na_2[Co(OH)_4]$ *violet-red*

$Ni(OH)_2$ *cannot be dissolved in alkali*

в) Me^{2+} salts are partially hydrolyzed.

$$Me^{2+} + HOH \rightleftarrows MeOH^{+} + H^{+}$$

$$MeOH^{+} + HOH \rightleftarrows Me(OH)_2 + H^{+}$$

They form a lot of complexes

$$Co(OH)_2 + 6NH_3 \rightleftarrows [Co(NH_3)_6](OH)_2$$ *yellow*

$$Ni(OH)_2 + 6NH_3 \rightleftarrows [Ni(NH_3)_6](OH)_2$$ *violet-blue*

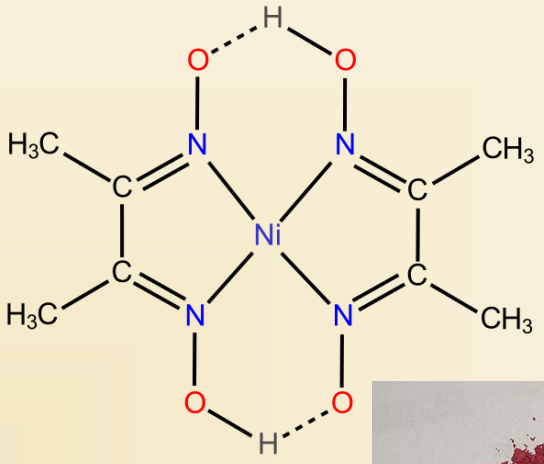
Ammonia complexes of iron (II), cobalt (II), nickel (II) are stable only in solid phase in the big excess of ammonia. These complexes are instable in water solutions.

$$[Fe(NH_3)_6]Cl_2 + 2H_2O \rightleftarrows Fe(OH)_2 + 4NH_3 + 2NH_4Cl$$

$K_4[Fe(CN)_6]$ – ***«yellow (gold) blood salt»***

To check the presence of Ni^{2+} in a solution they use dimethylglyoxim

$$2\ \begin{matrix} H_3C-C=N-OH \\ | \\ H_3C-C=N-OH \end{matrix} + Ni^{2+} + 2NH_3 \rightarrow$$



Fe^{2+} salts are easily oxidized by oxygen in neutral medium up to basic salts

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4$$

In acidic medium Fe^{2+} salts are oxidized up to normal salts Fe^{3+}

$$4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O$$

Mohr's salt is more stable against oxidation by oxygen from the air then other Fe^{2+} salts

$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, than $FeSO_4 \cdot 7H_2O$

COMPOUNDS WITH IRON FAMILY ELEMENTS IN THE OXIDATION STATE OF +3

The most stable oxidation state of iron is +3. There are many complexes with Fe^{+3} and Co^{+3}, but for Ni^{+3} just a few complexes are known.

a) Oxides Me_2O_3

Fe_2O_3 is stable; while Ni_2O_3 and Co_2O_3 are instable and decompose in normal conditions

$$6Co_2O_3 \rightarrow O_2 + 4Co_3O_4$$

Fe_2O_3 can be dissolved in acids

$$Fe_2O_3 + 6HCl + 9H_2O \rightarrow 2[Fe(H_2O)_6]Cl_3$$

Ni_2O_3 and Co_2O_3 demonstrate oxidative properties.

$$Ni_2O_3 + 6HCl \rightarrow 2NiCl_2 + Cl_2 + 3H_2O$$

$$2Ni_2O_3 + 4H_2SO_4 \rightarrow 4NiSO_4 + O_2 + 4H_2O$$

Fe_2O_3 demonstrates acidic properties when it reacts with alkalis or carbonates of alkali metals at high temperature in the melt. As a result, ferrites are formed:

$$Na_2CO_3 + Fe_2O_3 \xrightarrow{t} 2NaFeO_2 + CO_2\uparrow$$

$$2NaOH + Fe_2O_3 \xrightarrow{t} 2NaFeO_2 + H_2O$$

b) You can write $Me(OH)_3$ or $MeO(OH)$

$$Me^{3+} + 3OH^- \rightarrow MeO(OH) + H_2O$$

$$2Co(OH)_2 + NaClO \rightarrow 2CoO(OH)\downarrow + NaCl + H_2O$$

$$2Ni(OH)_2 + Br_2 + 2NaOH \rightarrow 2NiO(OH)\downarrow + 2NaBr + 2H_2O$$

Acidic and basic properties of Co^{3+} metahydroxyde are not studied well, since it is a strong oxidizer:

$$2CoO(OH) + 6HCl \rightarrow 2CoCl_2 + Cl_2\uparrow + 4H_2O$$

$$4CoO(OH) + 4H_2SO_4 \rightarrow 4CoSO_4 + O_2 + 6H_2O$$

or

$$4Co(OH)_3 + 4H_2SO_4 \rightarrow 4CoSO_4 + O_2 + 10H_2O$$

NiO(OH) reacts in the similar way.

NiO(OH) and CoO(OH) cannot react with water solutions of alkali, while FeO(OH) can be dissolved in concentrated water solutions of alkali. The product is hexahydroxyferrate (III) anion.

$$H_2O + FeO(OH) + 3NaOH_{conc.} \rightarrow Na_3[Fe(OH)_6]$$

In the melt: $Fe(OH)_3 + NaOH \xrightarrow{t} NaFeO_2 + 2H_2O$

sodium ferrite

c) **Salts of Me^{3+}** are oxidizers. Co^{3+} can even oxidize water.

$$4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + 4H^+ + O_2$$

or

$$4CoCl_3 + 2H_2O \rightarrow 4CoCl_2 + 4HCl + O_2$$

Salts of Fe^{3+} – $FeCl_3 \cdot 6H_2O$, $NH_4Fe(SO_4)_2 \cdot 12H_2O$

Salts of Fe^{3+} are partially hydrolyzed (stronger than Fe^{2+})

$$Fe^{3+} + HOH \rightleftarrows Fe(OH)^{2+} + H^+;$$

$$Fe(OH)^{2+} + H_2O \rightleftarrows Fe(OH)_2^+ + H^+;$$

$$Fe(OH)_2^+ + H_2O \rightleftarrows Fe(OH)_3 + H^+.$$

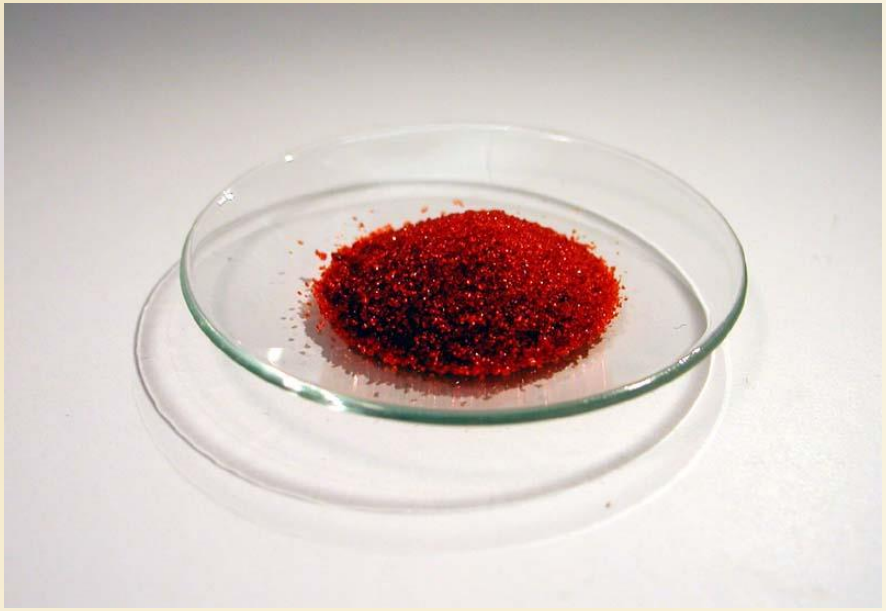
Test reaction for Fe^{3+}:

$$FeCl_3 + K_4[Fe(CN)_6] \rightarrow KFe[Fe(CN)_6]\downarrow + 3KCl$$

«gold blood salt» *Prussian blue*

«Gold» is a word from 4 letters, so there are 4 atoms of potassium in the formula of gold blood salt $K_4[Fe(CN)_6]$.

«Red» is a word from 3 letters, so there are 3 potassium atoms in the formula of red blood salt $K_3[Fe(CN)_6]$.



Test reactions for Fe^{3+}

Test reaction for Fe^{3+}

$KSCN + Fe^{3+} \rightarrow$ *several complex anions*

from $[Fe(SCN)]^{2+}$ to $[Fe(SCN)_6]^{3-}$

But a simplified equation is as follows:

$FeCl_3 + 3KSCN \rightleftarrows Fe(SCN)_3 + 3KCl$

Test reaction for Fe^{2+}

$$K_3[Fe(CN)_6] + Fe^{2+} \rightarrow KFe[Fe(CN)_6] + 2K^+$$

Prussian blue

Test reactions for Fe^{2+}

COMPOUNDS OF IRON
IN THE OXIDATION STATE OF +6: FERRATES

Fe, in contrast to Co and Ni, can demonstrate an oxidation state of +6.

FeO_3 and ferric acid (H_2FeO_4) are unknown, while corresponding salts are studied well:

$$2Fe(OH)_3+4NaOH+3NaClO = 3NaCl + 5H_2O + 2Na_2FeO_4$$

$$Fe + KClO_3 + 2KOH = KCl + К_2FeO_4 + H_2O$$

$$2Fe(OH)_3+10NaOH+3Br_2 \rightarrow 2Na_2FeO_4 + 6NaBr + 8H_2O$$

or

$$2FeO(OH)+10NaOH+3Br_2 \rightarrow 2Na_2FeO_4+6NaBr+6H_2O$$

Ferrates are violet-red solid substances that are decomposed at high temperature:

$$4K_2FeO_4 \xrightarrow{100-200^0C} 4KFeO_2 + 2K_2O + 3O_2$$

potassium ferrite

H_2FeO_4 **decomposes immediately after formation**

$$4H_2FeO_4 \rightarrow 2Fe_2O_3 + 3O_2 + 4H_2O$$

Ferrates are strong oxidizers, especially in the acidic medium. They oxidize water stronger than $KMnO_4$ **or** $K_2Cr_2O_7$**.**

$$4Na_2FeO_4 + 6H_2O \rightarrow 4FeO(OH) + 8NaOH + 3O_2$$

or

$$2Na_2FeO_4 + 10H_2O \rightarrow 4Fe(OH)_3 + 4NaOH + O_2$$

Ammonia can be oxidized by ferrates to nitrates

$$3NH_3+8K_2FeO_4+14H_2O = 3KNO_3 + 8Fe(OH)_3 + 13\ KOH$$

IRON *IS AN ESSENTIAL ELEMENT*

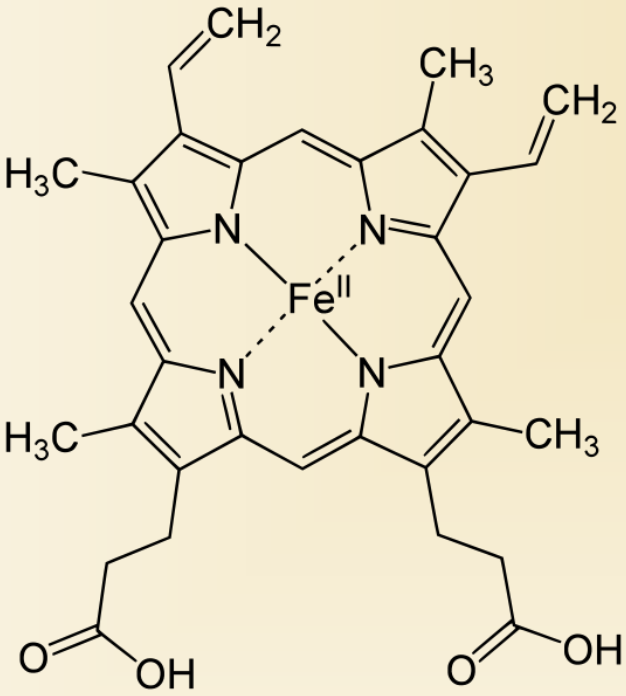
Iron containing proteins are: ***hemoglobin, myoglobin, ferritine, transferrine, lactoferrine.***

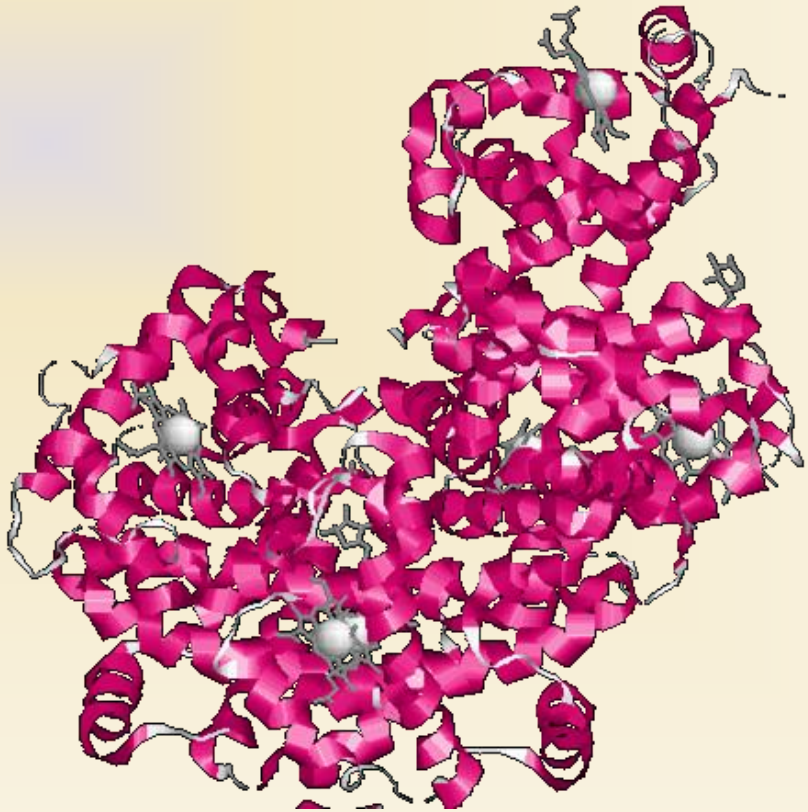
Enzymes: ***cytochromes, catalase, peroxidase.***

The excess of iron is known as – hypersyderosis – a professional disease associated with weakness, weight loss, nausea, vomiting and, finally, liver failure.

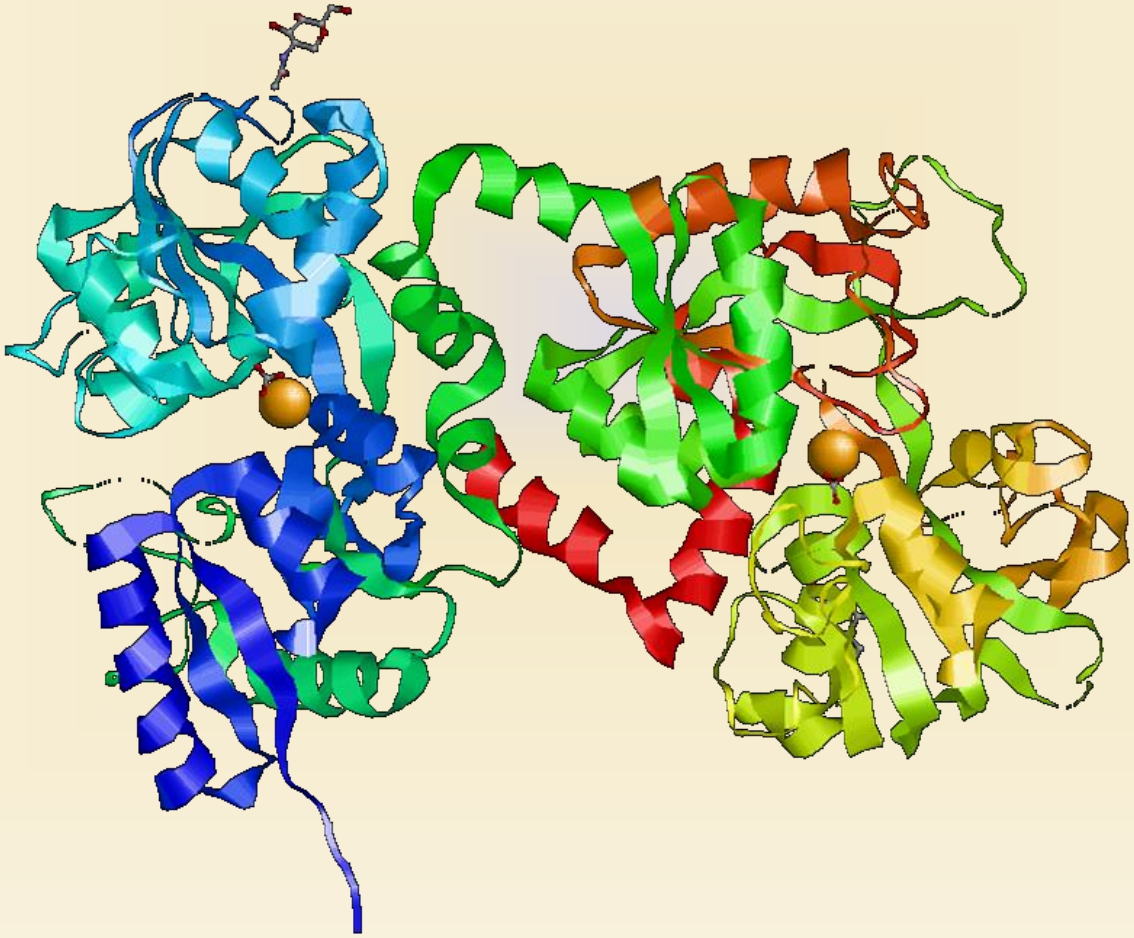
The lack of Fe **– is called hyposyderosis, anemia: weakness, breathlessness, fast heart beat rate.**

The treatment includes: – salts of Fe^{2+}($FeCl_2$, $FeSO_4$, $FeCO_3$, ascorbate, lactate, sorbate).





Lactoferrine



IRON CONTAINING SUBSTANCES USED IN PHARMACEUTICAL ANALYSIS

1. $K_4[Fe(CN)_6]$ – to check the presence of Zn^{2+} in medicines

$$3Zn^{2+} + 2K^+ + 2[Fe(CN)_6]^{4-} \rightarrow K_2Zn[Fe(CN)_6]\downarrow$$

white

as well as Cu^{2+}:

$$2Cu^{2+} + [Fe(CN)_6]^{4-} \rightarrow Cu_2[Fe(CN)_6]\downarrow$$

red-brown

2. Iron reduces Cu^{2+} from aquatic complexes

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu$$

Sodium nitroprusside

$Na_2[Fe(CN)_5NO]\cdot 2H_2O$ is a test reactant for $S_2O_3^{2-}$.
Resulting compound is blue.

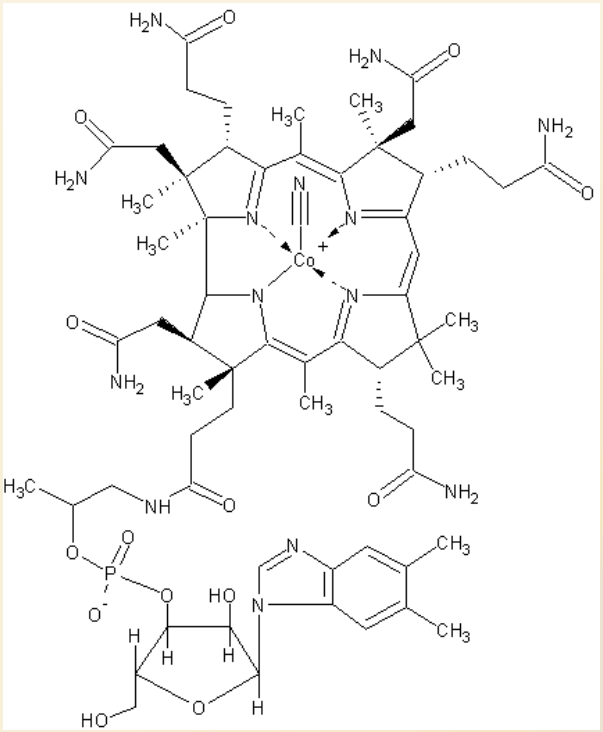
SO_3^{2-} - forms a red substance with sodium nitroprusside

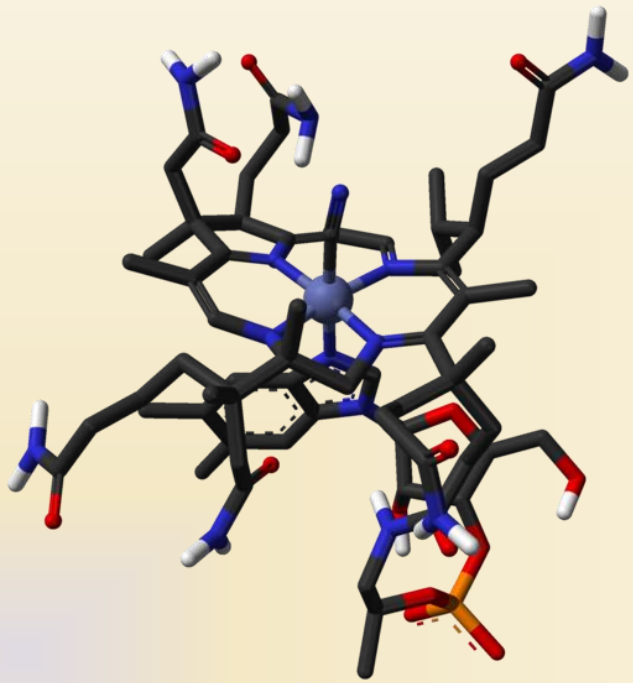
S^{2-} - forms a product of violet-red color with sodium nitroprusside:

$Na_2S + Na_2[Fe(CN)_5NO] = Na_4[Fe(CN)_5NOS]$

4. $Fe(SCN)_3$ reacts with fluorides:

$Fe(SCN)_3 + 6F^- = [FeF_6]^{3-} + 3SCN^-$





Cobalt **is essential for human body.**

Cobalt is a part of vitamin B_{12}, that is needed for hemopoesis.

Ni is also used by certain enzymes (like urease) as a co-factor.

Thank you for listening!