Overall characteristic of d-elements. Elements from groups IIIB – VIB and their compounds.

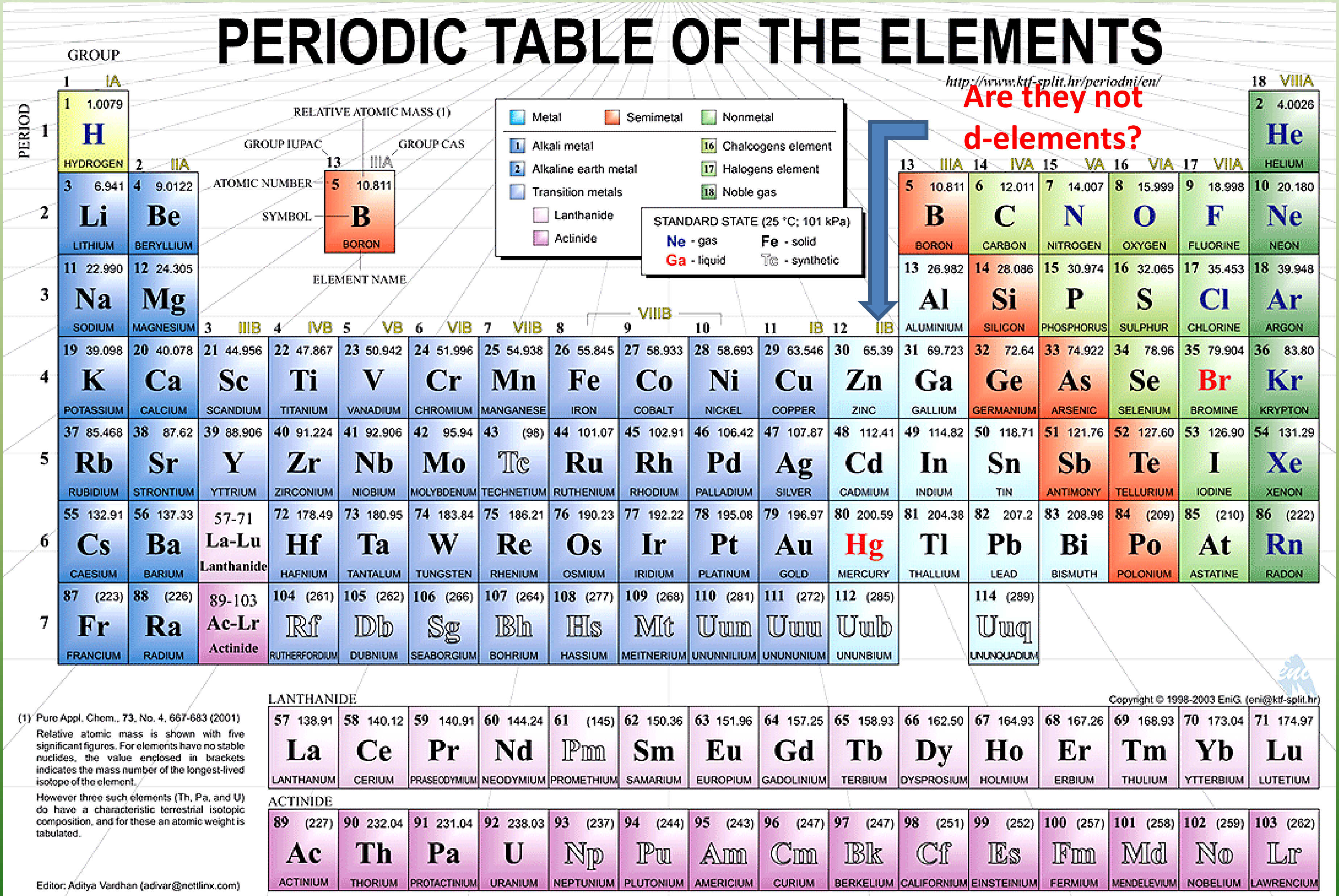
Lecture №3

The plan of the lecture:

- Terminological issues
- Overall characteristic of d-elements
- Chrome and its compounds
- Compounds of titanium
- Compounds of vanadium
- Compounds of molybdenum
- Compounds of tungsten

«d-elements» and «transition metals»

- **Transition metals** – are the elements in which the orbitals of the pre-outer shell are incomplete.
- According to this definition elements from IIB group are not classified as d-elements.



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

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2	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
3	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
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5	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
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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

RELATIVE ATOMIC MASS (1)
GROUP IUPAC 13
GROUP CAS IIIA
ATOMIC NUMBER 5
10.811
SYMBOL B
BORON
ELEMENT NAME

🟦 Metal
🟥 Semimetal
🟩 Nonmetal
1 Alkali metal
2 Alkaline earth metal
Transition metals
Lanthanide
Actinide
16 Chalcogens element
17 Halogens element
18 Noble gas

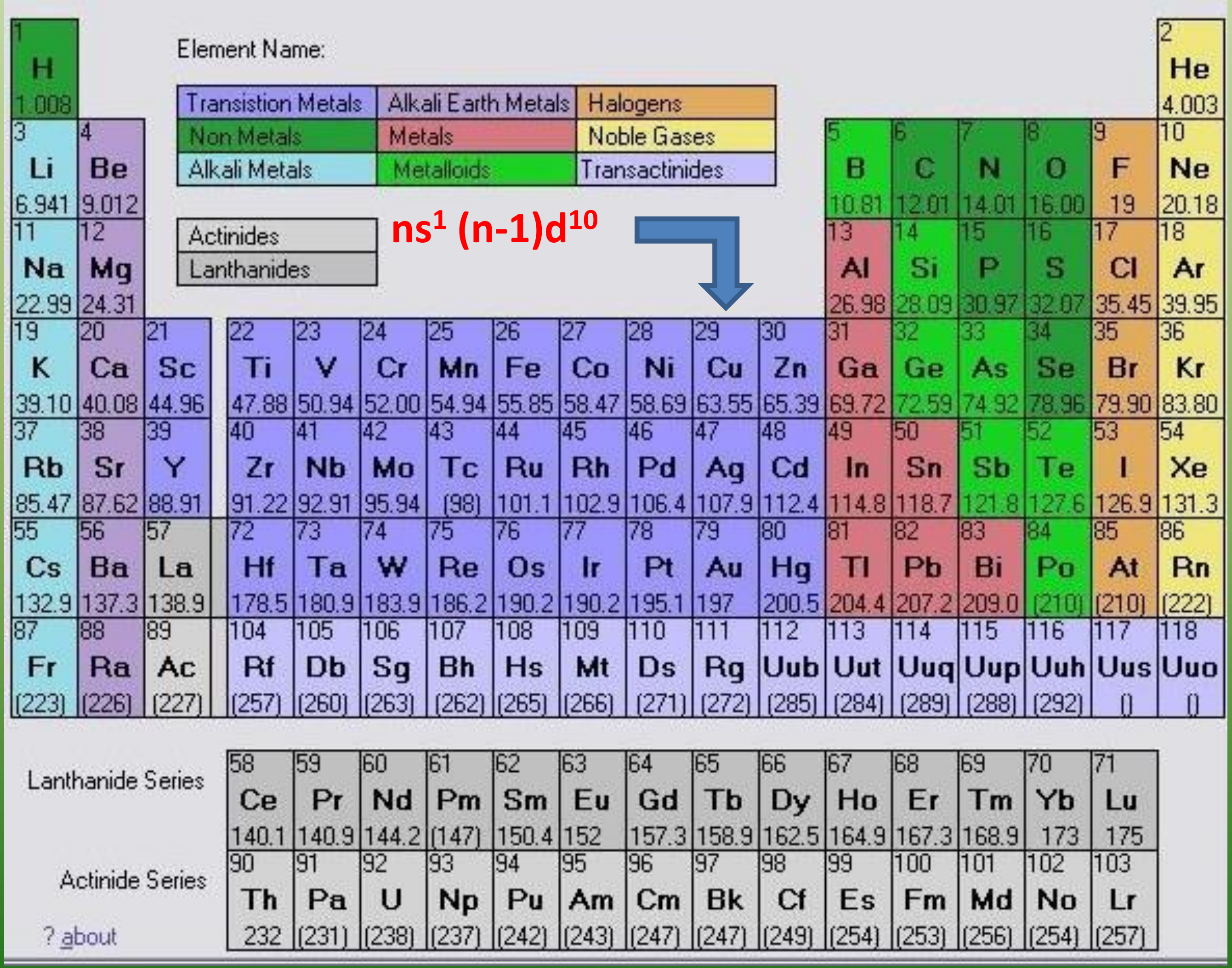
STANDARD STATE (25 °C; 101 kPa)
Ne - gas
Fe - solid
Ga - liquid
Tc - synthetic

(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)

Are they not d-elements?

Elements from IB group also have completed d-sublevels in the ground state



Element Name:

Transistion Metals	Alkali Earth Metals	Halogens
Non Metals	Metals	Noble Gases
Alkali Metals	Metalloids	Transactinides

Actinides
Lanthanides

$ns^1 (n-1)d^{10}$

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.47	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 190.2	78 Pt 195.1	79 Au 197	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (271)	111 Rg (272)	112 Uub (285)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (292)	117 Uus ()	118 Uuo ()

Lanthanide Series	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175
Actinide Series	90 Th 232	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)

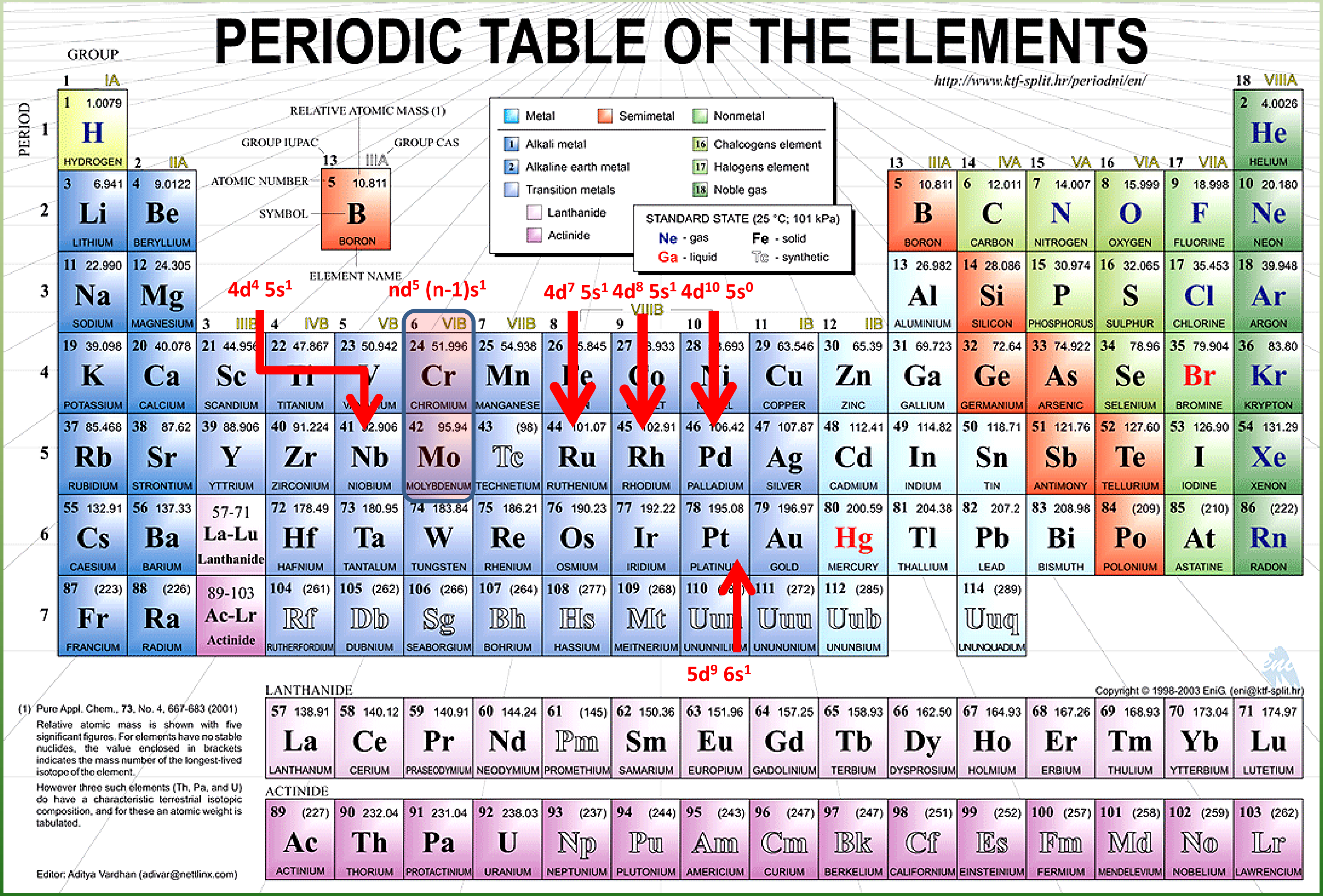
? about

According to the IUPAC definition, d-elements are those which are described by at least one from the two of the following sentences:

- In **the ground state** they have incomplete d-sublevel of the pre-outer level
- d-sublevel in these elements is incomplete in **one of the characteristic oxidation states**

*It is better to use a term «**d-block**»*

Ground state electron configurations with "shifts"



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☐ Actinide

16 Chalcogens element

17 Halogens element

18 Noble gas

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Ga - liquid Tc - synthetic

4d⁴ 5s¹

nd⁵ (n-1)s¹

4d⁷ 5s¹ 4d⁸ 5s¹ 4d¹⁰ 5s⁰

5d⁹ 6s¹

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Lanthanide contraction

- Atomic radii stay almost the same in elements from the same period in d-block.
- In f-elements from the 6th period atomic radii are almost the same as those in d-elements from the 5th period.
- Heavy d-elements are inert.
- In B-groups the activity of metals decreases if we go from top to bottom of the periodic table.

Lanthanide contraction

- For example, in VIB group the most active metal is chrome (it can be dissolved in dilute sulfuric and nitric acids).
- Molybdenum can be dissolved only in concentrated nitric acid.
- Tungsten can be dissolved only in the mixture of nitric and hydrofluoric acids.

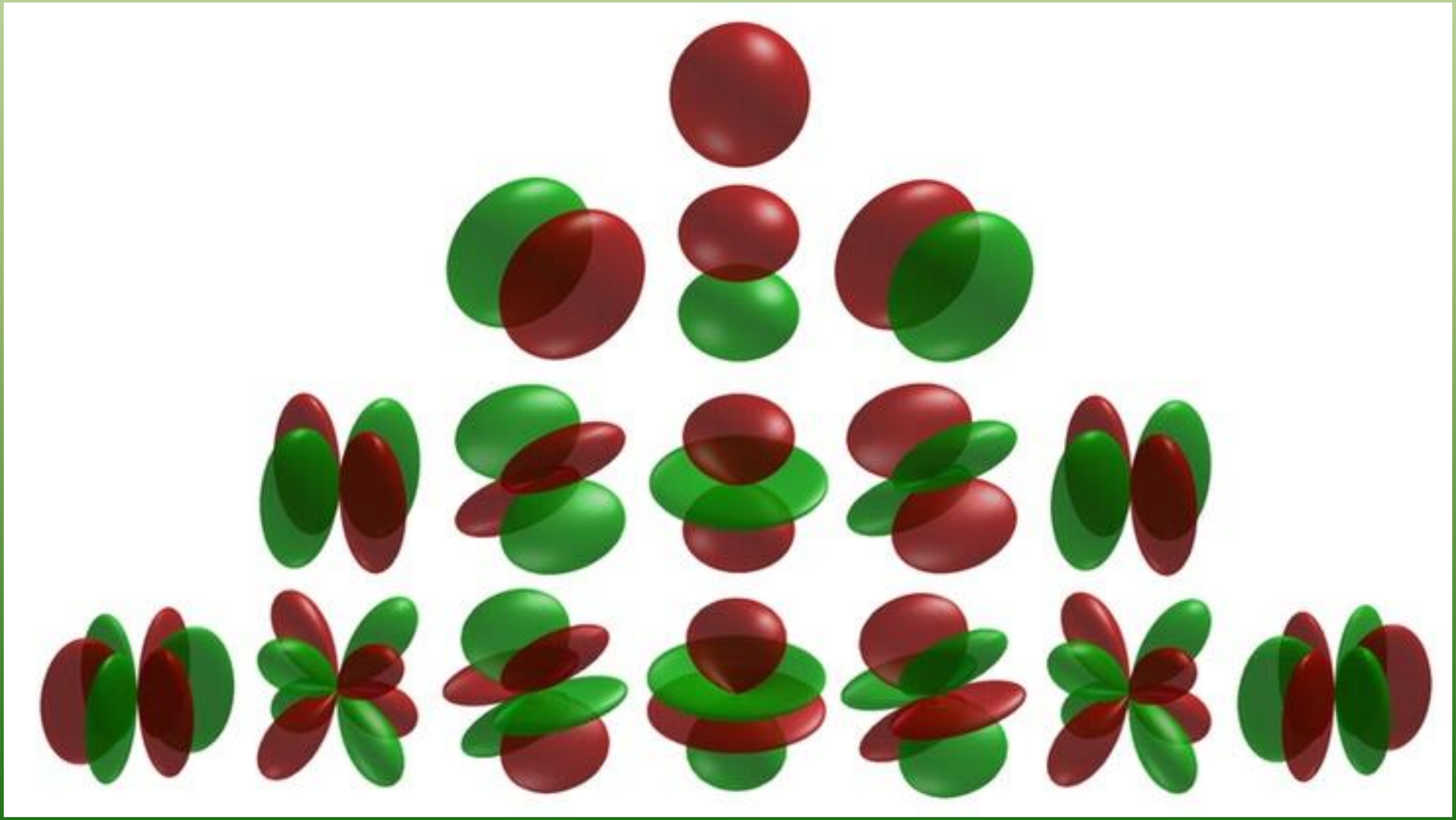
Atomic radii of d-elements

4th period	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
	162 pm	147 pm	134 pm	128 pm	127 pm	126 pm	125 pm	124 pm	128 pm	134 pm
5th period	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	180 pm	160 pm	146 pm	139 pm	136 pm	134 pm	134 pm	137 pm	144 pm	151 pm
6th period	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	187 pm	159 pm	146 pm	139 pm	137 pm	135 pm	136 pm	139 pm	144 pm	151 pm

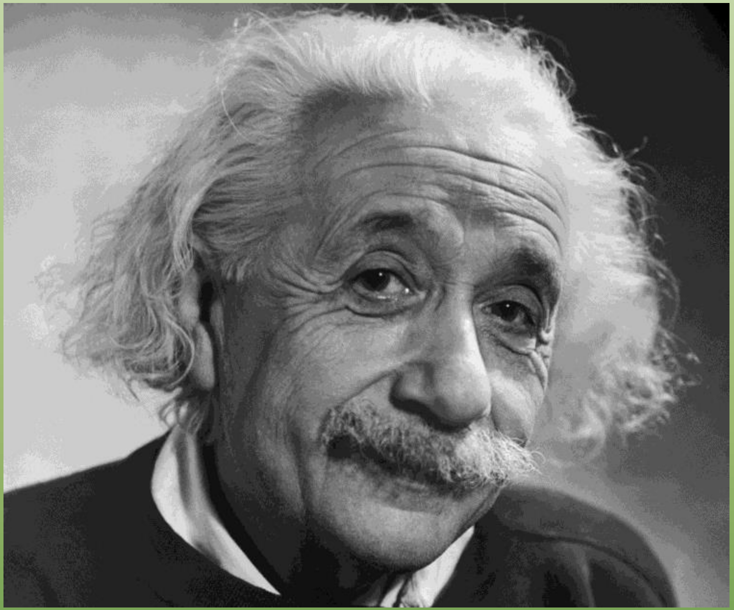
The difference between radii of d-elements from 5th and 6th periods is not significant, 2±1,4 pm (P=0,13)

Hypothesis about the weak shielding effect of d- and f-electrons

s > p > d >f



The theory of relativity



$$E = mc^2$$

The higher the charge of nucleus, the faster the movement of electrons

The closer the speed of electron to the speed of light, ***the heavier its mass***

Valence of d-elements

- For the first five d-elements from the 4th period the highest valence is equal to the group number (the sum of 4s and 3d electrons).
- For the last five d-elements the highest valence decreases by one if we move from left to right along the period because of the appearance of paired electrons on d-orbitals.

d-elements are prone to form complex compounds

- ns, np and (n-1)d orbitals have close energies. Because of this 9 orbitals can be involved in the formation of bonds (1 – s, 3 – p, 5 – d).
- Usually coordination numbers of d-elements vary from 2 to 6.
- Moreover, vacant nd orbitals may also participate in the formation of coordination bonds.

Reactions of complexation

- $ZnSO_4 + 4NaOH = Na_2[Zn(OH)_4] + Na_2SO_4$
- $ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4$
- $Zn(OH)_2 + 2NaOH = Na_2[Zn(OH)_4]$

- $CrCl_3 + 6NaOH = Na_3[Cr(OH)_6] + 3NaCl$
- $CrCl_3 + 3NaOH = Cr(OH)_3 + 3NaCl$
- $Cr(OH)_3 + 3NaOH = Na_3[Cr(OH)_6]$

Reactions of complexation

- $2KI + Hg(NO_3)_2 = HgI_2 + 2KNO_3$
- $2KI + HgI_2 = K_2[HgI_4]$

- $6KCN + FeSO_4 = K_4[Fe(CN)_6] + K_2SO_4$
- $12KCN + Fe_2(SO_4)_3 = 2K_3[Fe(CN)_6] + 3K_2SO_4$

- $Co(NO_2)_3 + 3NaNO_2 = Na_3[Co(NO_2)_6]$

- $NiSO_4 + 6NH_4OH = [Ni(NH_3)_6]SO_4 + 6H_2O$

The color of compounds containing d-elements

- Water solution of a compound of d-element is colored if the cation of that metal has at least one unpaired electron.

- The color of **hydrated ion (aquatic complex)** appears due to the absorption of light at the corresponding wave length by ***unpaired electrons*** and their transitions to the excited state.

Colors of water solutions of salts of some d-elements

Ion	Color	Electron configuration of atom						Electron configuration of ion					
Ti^{3+}	violet-red	$4s^2$	$3d^2$					$4s^0$	$3d^1$				
		↑↓	↑	↑					↑				
Mn^{2+}	pale-pink	$4s^2$	$3d^5$					$4s^0$	$3d^5$				
		↑↓	↑	↑	↑	↑	↑		↑	↑	↑	↑	↑
Fe^{2+}	green	$4s^2$	$3d^6$					$4s^0$	$3d^6$				
		↑↓	↑↓	↑	↑	↑	↑		↑↓	↑	↑	↑	↑
Zn^{2+}	colorless	$4s^2$	$3d^{10}$					$4s^0$	$3d^{10}$				
		↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓	↑↓	↑↓	↑↓	↑↓
Ag^{+}	colorless	$4s^1$	$3d^{10}$					$4s^0$	$3d^{10}$				
		↑	↑↓	↑↓	↑↓	↑↓	↑↓		↑↓	↑↓	↑↓	↑↓	↑↓

The influence of the nature of ligand on the color of complex compounds of d-elements

- $[Cu(H_2O)_6]^{2+}$ - pale-blue
- $[Cu(NH_3)_4(H_2O)_2]^{2+}$ - violet

- $[CrCl_2(H_2O)_4]Cl$ - green
- $[Cr(H_2O)_6]Cl_3$ - violet

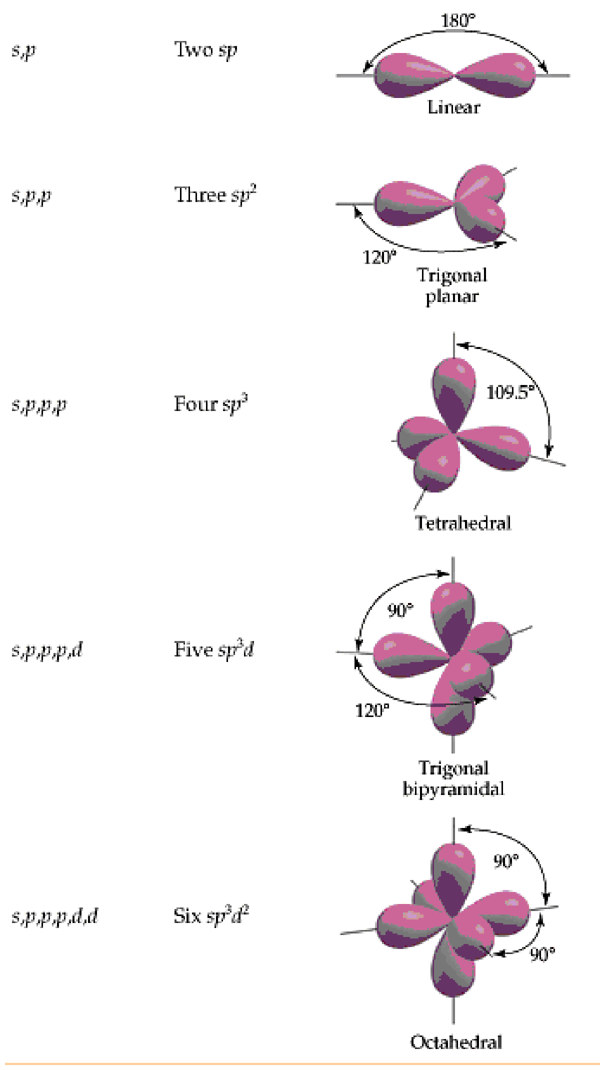
Oxides of d-elements

- In many cases oxides of d-elements are nonstoichiometric compounds.
- Sometimes they can be imagined as mixtures of oxides of the same metal in different oxidation states:
- $Fe_3O_4 = FeO \cdot Fe_2O_3$
- $3CrO_2 = Cr_2O_3 \cdot CrO_3$
- $4VO_2 = V_2O_3 \cdot V_2O_5$

Hydroxides of d-elements

- Hydroxides and oxides in which d-elements demonstrate the lowest oxidation state are basic.
- CrO $Cr(OH)_2$
- Hydroxides and oxides in which d-elements demonstrate the highest oxidation state are acidic.
- CrO_3 $H_2Cr_2O_7$
- Hydroxides and oxides in which d-elements are in their intermediate oxidation states are amphoteric.
- Cr_2O_3 $Cr(OH)_3$ / $HCrO_2 \cdot H_2O$

Hybridization of d-orbitals



As a result of hybridization of d-orbitals, their shielding effect disappears

Valence electrons are attracted to the nucleus stronger then in the absence of hybridization

Bonds with nonmetals (including those with oxygen) become rather covalent, than ionic

Chrome

- Natural resources:
- Chromite: $FeO \cdot Cr_2O_3 = FeCr_2O_4$

  $Fe(CrO_2)_2$

- Crocoite: $PbO \cdot CrO_3 = PbCrO_4$

Passivation of chrome

- There is a protective layer of Cr_2O_3 on the surface of chrome that prevents its further oxidation.
- Because of this reason, the dissolving of chrome in non-oxidizing acids (HCl, HBr, HI, dilute H_2SO_4) proceeds slowly.
- The layer of oxide can be easily removed by a scratching.

Chemical properties of chrome

- Chrome reacts with oxygen at t°=2000°C
- $4Cr + 3O_2 \rightarrow 2Cr_2O_3$

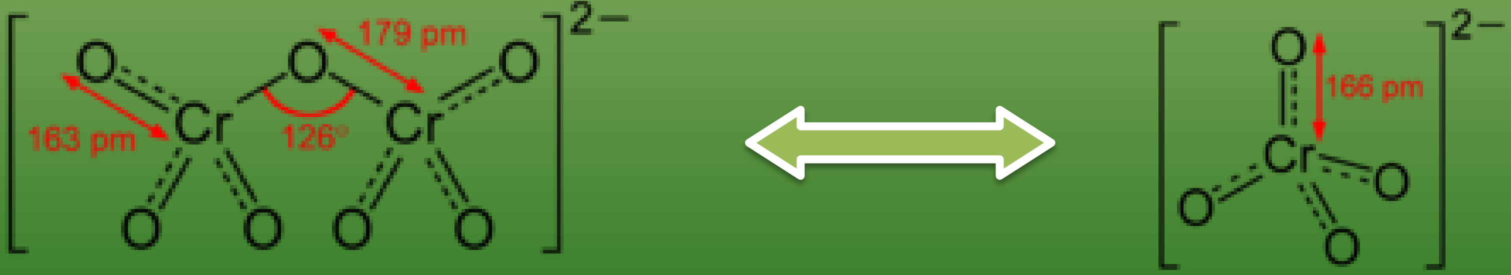
- Chrome forms nonstoichiometric compounds with many nonmetals:
- Cr_4C; Cr_7C_3; Cr_3C_2
- Cr_3Si; Cr_5Si; $CrSi_2$

Chemical properties of chrome

- $2Cr + 3H_2O\ (t°) \rightarrow Cr_2O_3 + 3H_2\uparrow$
- $Cr + H_2SO_4(dilute) \rightarrow CrSO_4 + H_2\uparrow$
- $12CrSO_4 + O_2 \rightarrow 4Cr_2(SO_4)_3 + 2Cr_2O_3$
- $Cr + 2HCl \rightarrow CrCl_2 + H_2\uparrow$
- $4CrCl_2 + O_2 + 4HCl \rightarrow 4CrCl_3 + 2H_2O$
- $2Cr + 6H_2SO_4(conc., t°) \rightarrow Cr_2(SO_4)_3 + 3SO_2\uparrow + 6H_2O$

Compounds of chrome

- Dichromates and chromates:
- $H_2O + Cr_2O_7^{2-} \leftrightarrow 2H^+ + 2CrO_4^{2-}$
- Dichromate + OH^- ↔ Chromate + H^+
- Orange ↔ yellow



Compounds of chrome

$$2HCrO_4^{-} \leftrightarrow Cr_2O_7^{2-} + H_2O$$

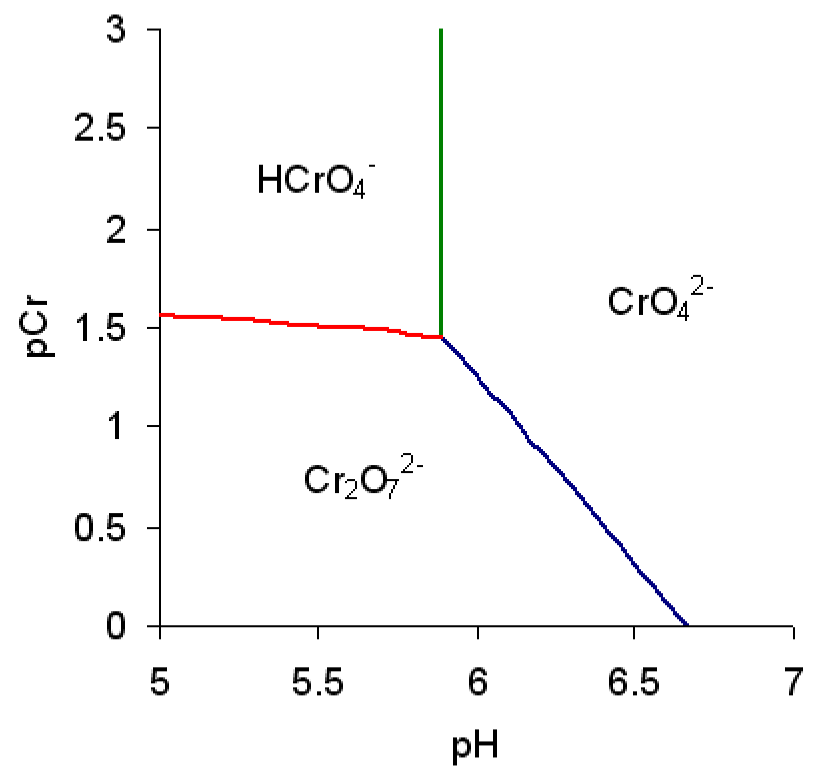
-Cr-O-H + H-O-Cr-

↓

-Cr-O-Cr

+

H_2O



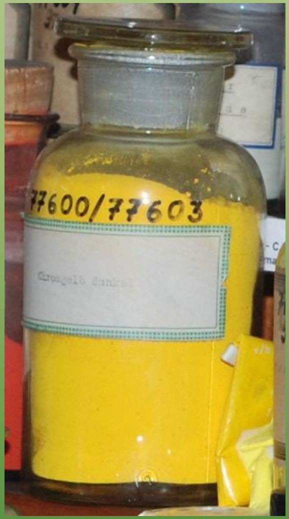
$$2CrO_4^{2-} + 2H^{+} \leftrightarrow 2HCrO_4^{-} \leftrightarrow Cr_2O_7^{2-} + H_2O$$

chromates ↔ dichromates

The usage of chrome containing compounds in pharmaceutical analysis

- Potassium chromate K_2CrO_4 forms yellow lead chromate with lead cations → $PbCrO_4\downarrow$

yellow



- $2PbCrO_4 + 4HNO_3(conc.) \rightarrow 2Pb(NO_3)_2 + H_2Cr_2O_7 + H_2O$
- $PbCrO_4 + 4KOH \rightarrow K_2[Pb(OH)_4] + K_2CrO_4$

The usage of chrome containing compounds in pharmaceutical analysis

- H_2CrO_4 – for cocaine detection
- $K_2Cr_2O_7$ – for dichromatometry

- $$3C_2H_5OH + \overset{orange}{K_2Cr_2O_7} + 4H_2SO_4 \rightarrow$$
  $$\rightarrow 3CH_3COH + K_2SO_4 + \underset{green}{Cr_2(SO_4)_3} + 7H_2O$$

- $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

- $$K_2Cr_2O_7 + 2AgNO_3 \rightarrow \underset{\text{dark-red}}{Ag_2Cr_2O_7\downarrow} + 2KNO_3$$

RedOx indicators

Indicator	Color		*E*°, V, at [H⁺]= = 1 mol/L
	Ind_{Red}	Ind_{Ox}	
Diphenylamine	Colorless	Violet	0.76
Diphenylbenzidine	Colorless	Violet	0.76
Diphenylbenzidine sulfonate of sodium	Colorless	Red-violet	0.84

Dichromates are strong oxidizers

$3K_2SO_3 + 4H_2SO_4 + K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3 + 4K_2SO_4 + 4H_2O$

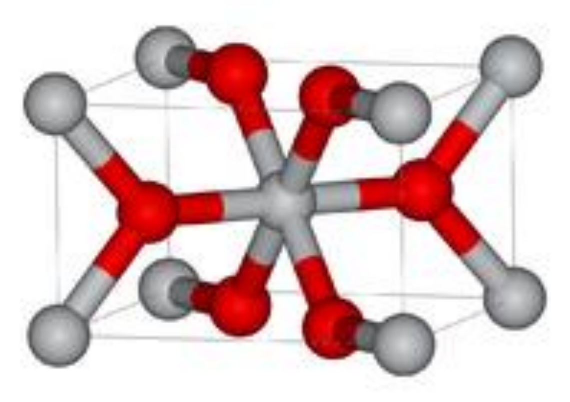
The usage of titanium, niobium and tantalum in surgery

- Alloys based on titanium are used for construction of artificial joints and implants for traumatology, orthopedy, dentistry. One of the alloys has the following content (in mass %): titanium 84%; niobium 7.5%; aluminum 6.5%; molybdenum 1.5%; tantalum 0.5%.

Artificial joints

Titanium dioxide

In TiO_2 lattice each Ti^{4+} is surrounded by six O^{2-}, while each O^{2-} is surrounded by three Ti^{4+}. It is not a typical lattice for ionic compounds.



$TiO_2 + 2H_2SO_4 \rightarrow Ti(SO_4)_2 + 2H_2O$

$TiO_2 + 2NaOH \rightarrow Na_2TiO_3 + H_2O$

$TiO_2 + K_2CO_3 \rightarrow K_2TiO_3 + CO_2\uparrow$

The usage of titanium dioxide in pharmacy

- TiO_2 – is used as an additive to polymers (polyethylene, polypropylene) with the aim to make them nonpermeable for light. Medicines covered by polymers with titanium dioxide are resistant to the light and can be stored not just in a dark place.

Zirconium bracer

- Zirconium doesn’t play significant biological roles. Both pure zirconium and its compounds are inert. So, zirconium bracers are harmless.

Vanadium is toxic

- Vanadium can disturb the synthesis of fatty acids and cholesterol. Vanadium inhibits many enzymes, disturbs phosphorylation and ATP synthesis because its oxide reacts with water and forms orthovanadic acid similar to orthophosphoric acid.
- $V_2O_5 + H_2O \rightarrow 2HVO_3$
- $HVO_3 + H_2O \rightarrow H_3VO_4$

V_2O_5 – is an amphotheric oxide

- $V_2O_5 + 2HNO_3 \rightarrow 2VO_2(NO_3) + H_2O$
- $V_2O_5 + 6HCl \rightarrow 2VOCl_2 + Cl_2 + 3H_2O$

- $V^{4+} + 2H_2O \rightarrow V(OH)_2{}^{2+} + 2H^+$
- $V(OH)_2{}^{2+} \rightarrow VO^{2+} + H_2O$
- $VO^{2+} + 5H_2O \rightarrow [VO(H_2O)_5]^{2+}$

The usage of ammonium metavanadate in pharmacy

- NH_4VO_3 – is a strong oxidizer that is used as a titrant with the aim to determine the concentration of reducers (**vanadatometry**), such as isoniazide (an antibiotic for the treatment of tuberculosis).

The usage of ammonium metavanadate in pharmacy

- $VO_3^- + 2H^+ + e \rightarrow VO_2 + H_2O$
- NH_4VO_3 – is the part of molybdenum vanadium reactant (MVR)

  $((NH_4)_2MoO_4 + NH_4VO_3)$ – is used for the detection of phosphates

PO_4^{3-} + MVR = yellow color

- VitB6 + NH_4VO_3 = blue-violet color

The usage of molybdenum in pharmacy

- ($(NH_4)_2MoO_4 + NH_4VO_3$) – is molybdenum vanadium reactant used for PO_4^{3-} detection

- $(NH_4)_2MoO_4$ – is used for detection of PO_4^{3-}, scopolamine
- $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \xrightarrow{} \textit{yellow}$ $(NH_4)_3PO_4 \cdot 12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$

- $H_3PO_4 \cdot 12MoO_3$ – phosphomolybdic acid, that is used for the detection of alkaloids

The usage of tungsten containing compounds in pharmacy

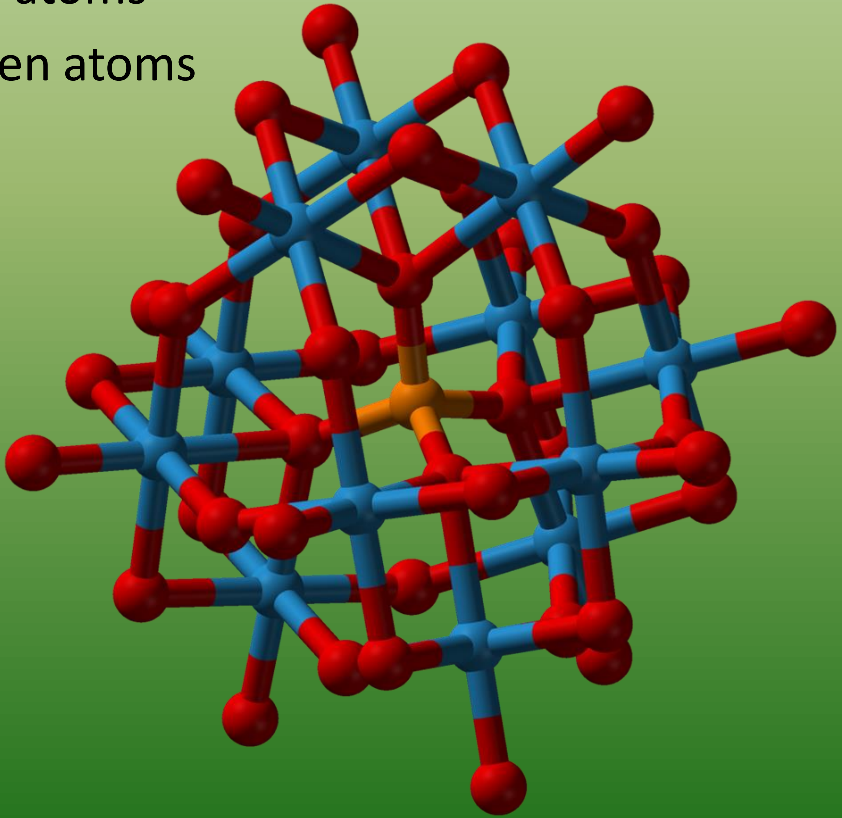
- $H_3PO_4 \cdot 12WO_3$ – phosphotungstic acid that is used for detection of alkaloids
- $H_8[Si(W_2O_7)_6]$ – silicotungstic acid that is also used for detection of alkaloids

Heteropolyacids

Heteropolyacids – are complex compounds of anionic type that contain anions of inorganic isopolyacids (molybdic, tungstic, vanadic, niobic and others) as ligands and a single central atom represented by P(V), As(V), Si(IV), Ge(IV), Ti(IV), Ce(IV).

Heteropolyacids

- Heteroatom = p-element
- Metal = d-element
- Oxygen atoms
- Hydrogen atoms



pH	Main ions
1,0	$[PW_{12}O_{40}]^{3-}$
2,2	$[PW_{12}O_{40}]^{3-}$, $[P_2W_{21}O_{71}]^{6-}$, $[PW_{11}O_{39}]^{7-}$
3,5	$[PW_{12}O_{40}]^{3-}$, $[P_2W_{21}O_{71}]^{6-}$, $[PW_{11}O_{39}]^{7-}$, $[P_2W_{18}O_{62}]^{6-}$, $[P_2W_{19}O_{67}]^{10-}$
5,4	$[P_2W_{21}O_{71}]^{6-}$, $[PW_{11}O_{39}]^{7-}$, $[P_2W_{18}O_{62}]^{6-}$
7,3	$[PW_9O_{34}]^{9-}$
8,3	PO_4^{3-}, WO_4^{2-}

The usage of cerium (IV) sulfate in pharmaceutical analysis

- $Ce(SO_4)_2$ – is a strong oxidizer that is used for titration of medicines which demonstrate reductive properties, such as H_2O_2, and ions: As^{3+}; I^-; Sb^{3+}; Mo^{5+}; Sn^{2+}; $S_2O_3^{2-}$; Tl^+; (**cerimetric titration**)

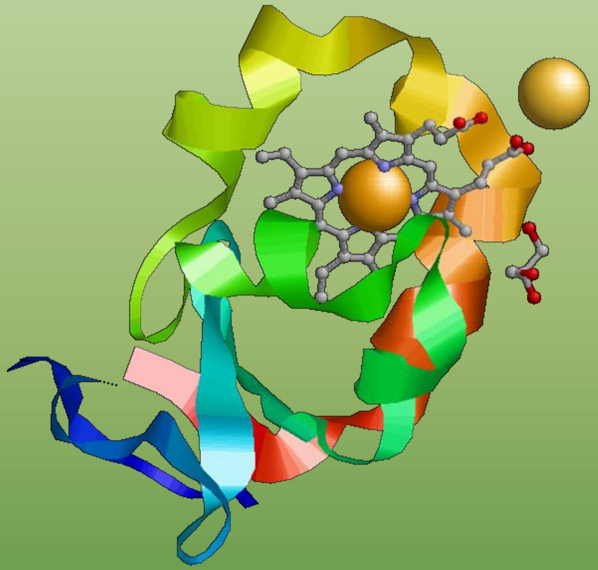
The usage of cerium (IV) sulfate in pharmaceutical analysis

- $Ce^{4+} + e \rightarrow Ce^{3+}$
- $2FeSO_4 + 2Ce(SO_4)_2 \rightarrow Fe_2(SO_4)_3 + Ce_2(SO_4)_3$
- Fe^{2+} + dipyridyl = red color
- $HCOH + 2Ce(SO_4)_2 + H_2O \rightarrow$

$$HCOOH + Ce_2(SO_4)_3 + H_2SO_4$$

Aspirin, phenol, paracetamol, vitamins E and K can be titrated as well.

Molybdoptherine



Molybdoptherine is a co-factor of a few enzymes, including human sulfite reductase

«Volcano»

$(NH_4)_2Cr_2O_7$ (t°) $\rightarrow Cr_2O_3 + N_2\uparrow + 4H_2O$

Thank you for listening!