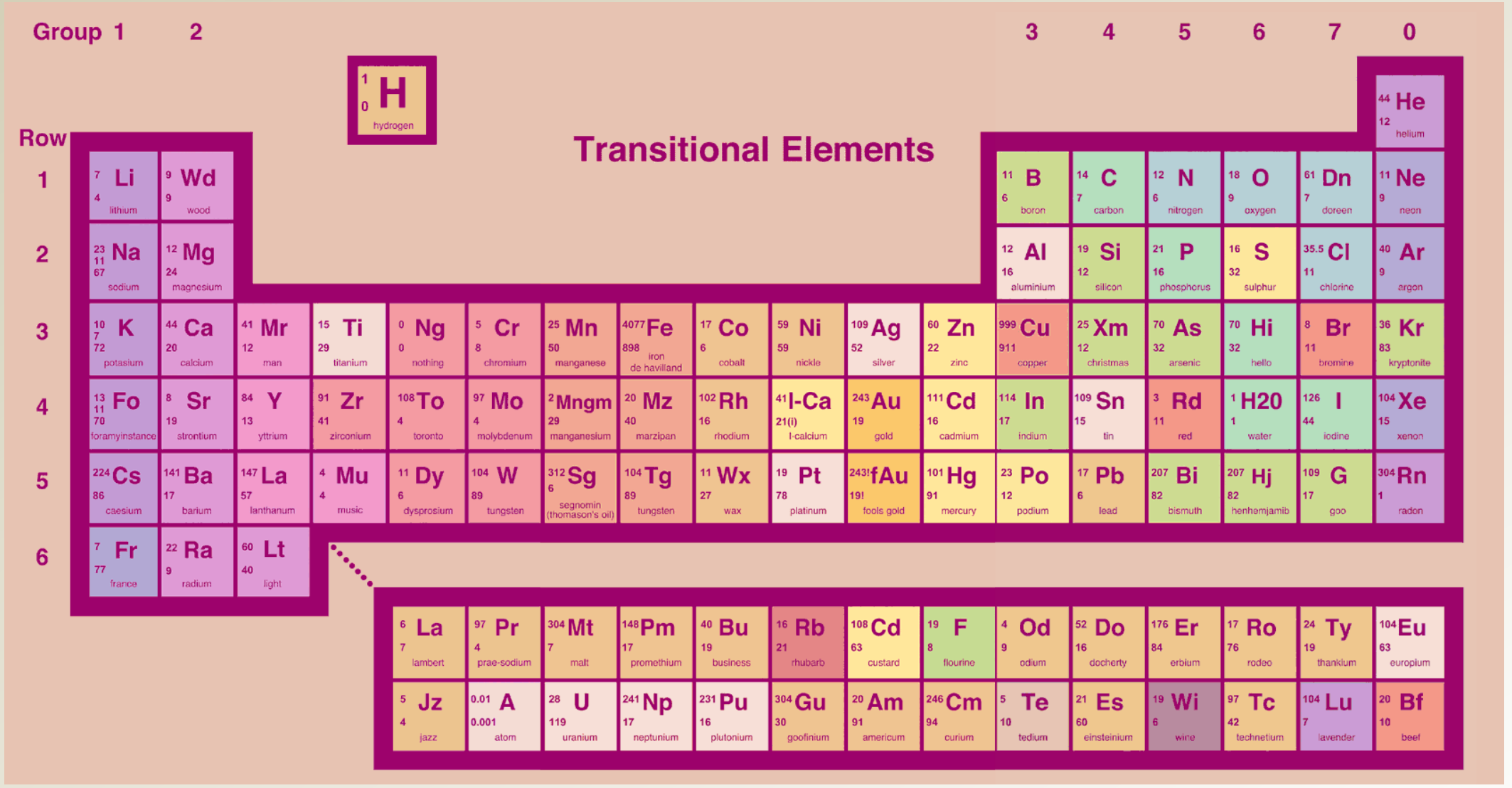
ANORGANSKA KEMIJA 2



Kako do ocjene?

Dva (2) kolokvija

Pismeni ispit

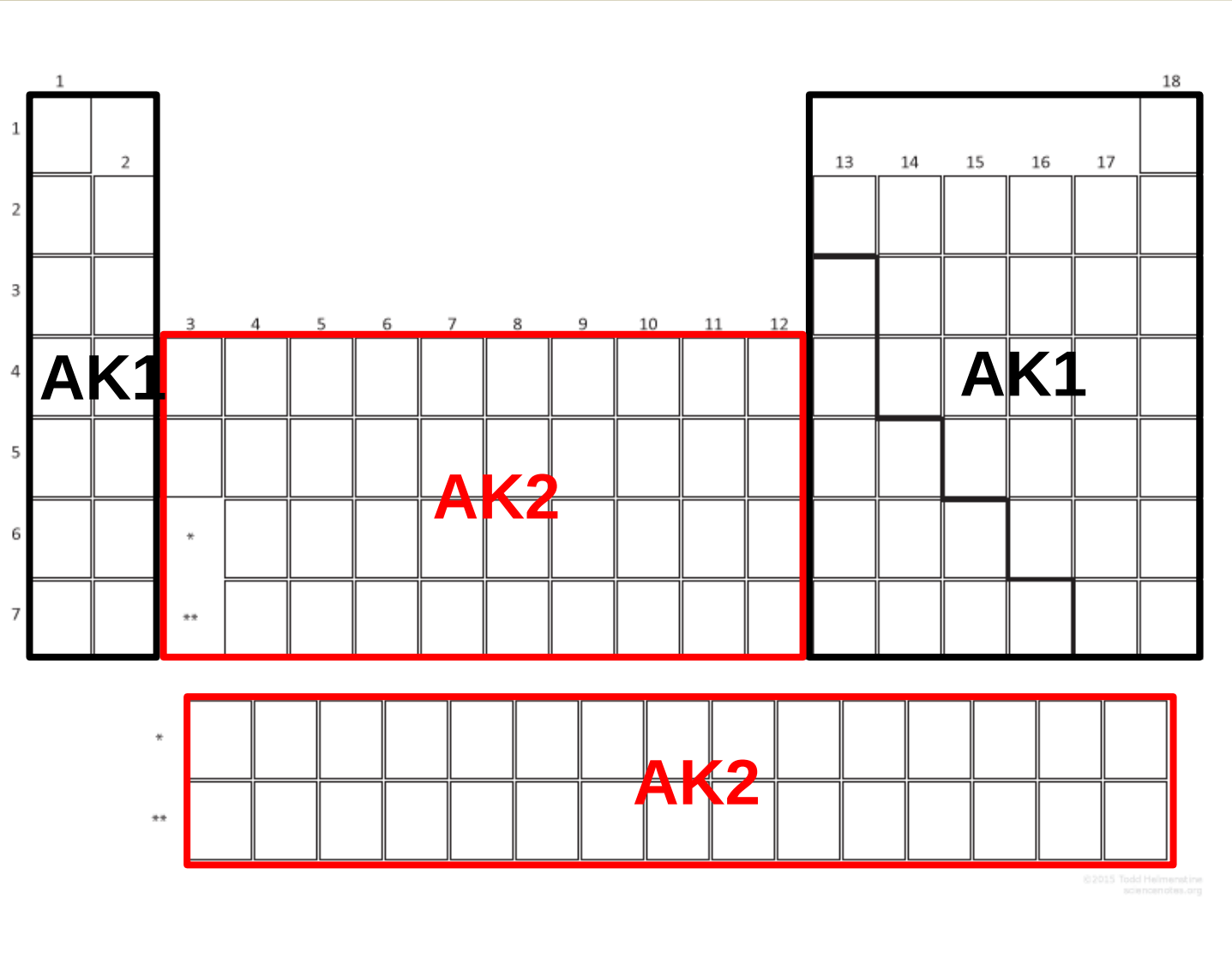
Usmeni ispit

TERMINI KOLOKVIJA
1. KOLOKVIJ: 28. IV. 2019. PREDAVAONICA A2 14-17
2. KOLOKVIJ 9. VI. 2020. PREDAVAONICA A2 14-17

Prolazak na oba kolokvija = oslobađanje od (prvog) pismenog ispita

Neizlazak na kolokvij / pad na oba kolokvija = detaljniji usmeni ispit

ANORGANSKA KEMIJA 2



AK2 – skakutanje kroz prijelazne elemente:

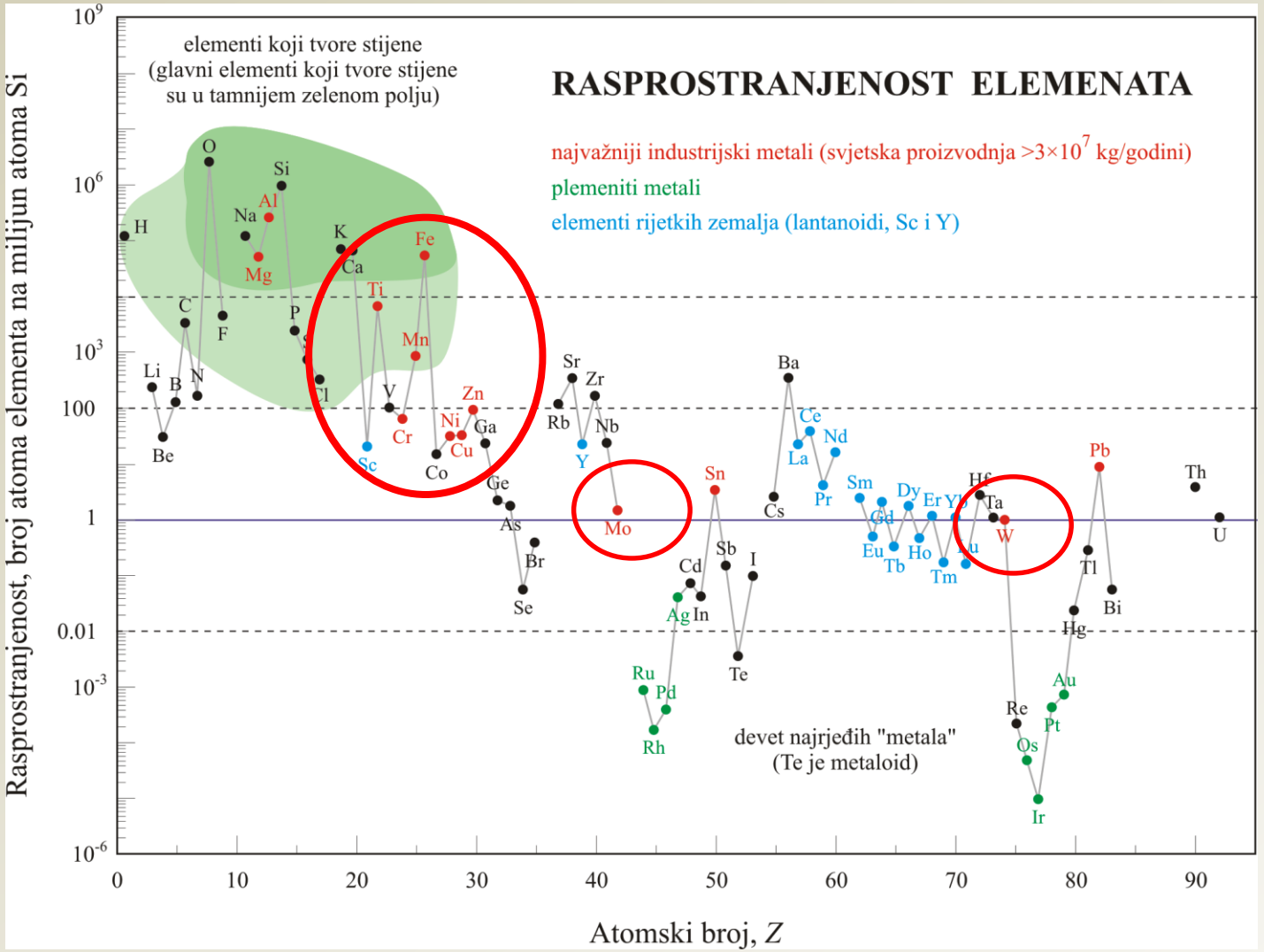
1. Metali i metalna veza
2. Teorije koordinacije
3. Magnetska svojstva spojeva
4. Kiselo-bazna svojstva iona
5. Detaljnije upoznavanje s najvažnijim elementima i skupinama elemenata

ELEMENTI d- i f- BLOKA

PRIJELAZNI ELEMENTI 3.-11.

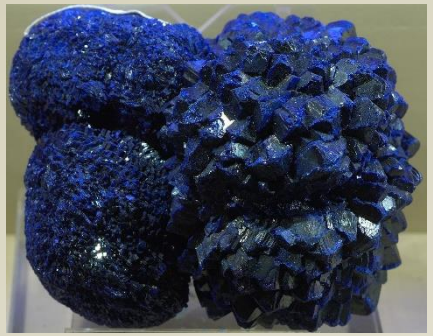
	3	4	5	6	7	8	9	10	11	12
	3B	4B	5B	6B	7B	⌐ 8B ¬			1B	2B
1.	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
2.	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
3.	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 **Ds**	111 **Rg**	112 **Cn**

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr


RASPROSTRANJENOST ELEMENATA
najvažniji industrijski metali (svjetska proizvodnja >3×10^7 kg/godini)
plemeniti metali
elementi rijetkih zemalja (lantanoidi, Sc i Y)
elementi koji tvore stijene
(glavni elementi koji tvore stijene
su u tamnijem zelenom polju)
devet najrjeđih "metala"
(Te je metaloid)
Raspostranjenost, broj atoma elementa na milijun atoma Si
Atomski broj, Z
10^9
10^6
10^3
100
1
0.01
10^-3
10^-6
0
10
20
30
40
50
60
70
80
90
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
Cl
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Y
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

AK 2 – KEMIJA U BOJI

AZURIT $Cu_3(CO_3)_2(OH)_2$



MALAHIT $Cu_2(CO_3)(OH)_2$

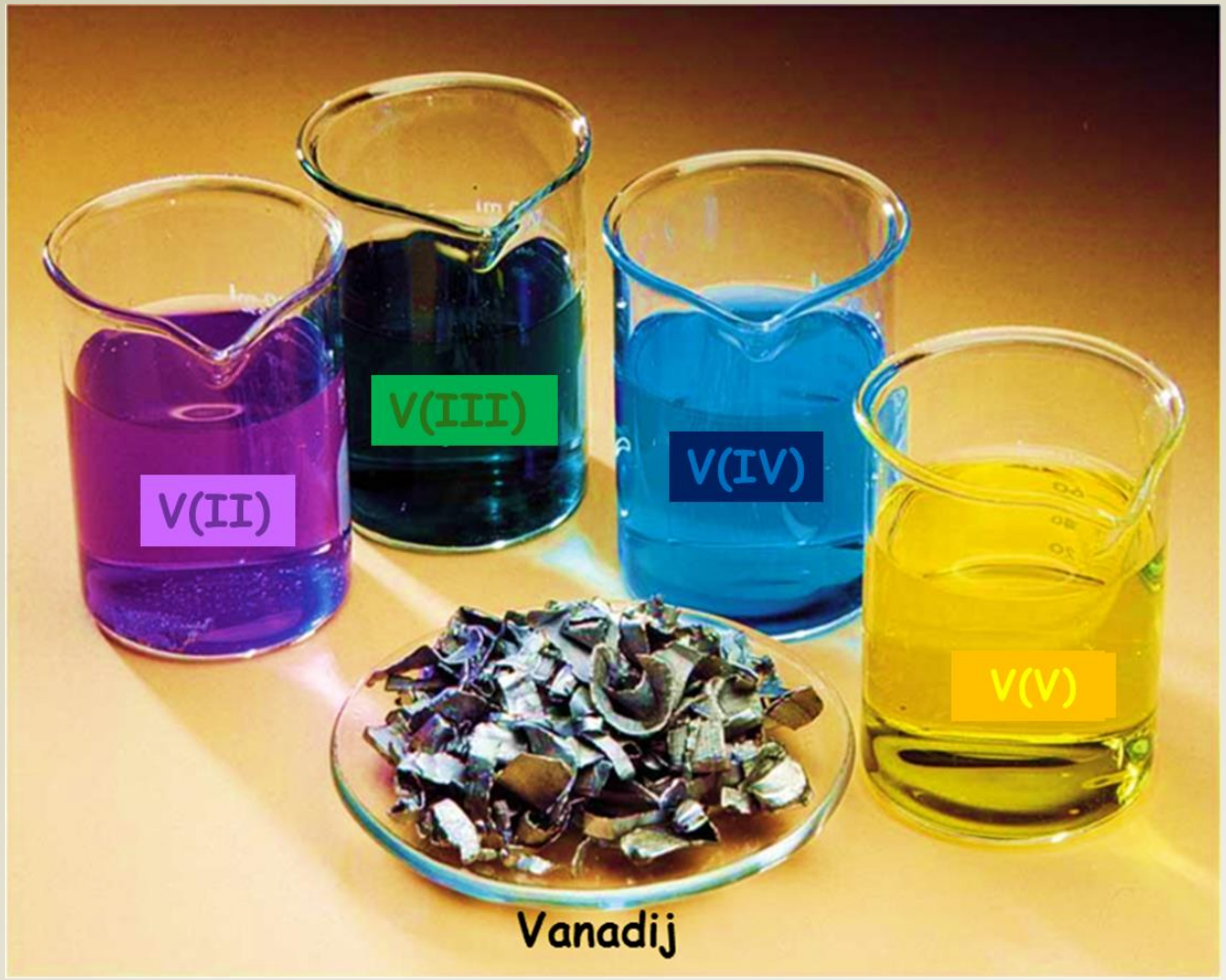
$2\ Cu_3(CO_3)_2(OH)_2 + H_2O \rightarrow 3\ Cu_2(CO_3)(OH)_2 + CO_2$

„Osnovna svrha anorganske kemije je pripravljanje šarenih kristalića u raznim bojama”

T. Friščić, ca. 2000.

$Cu_2CO_3(OH)_2 + 8\ SiO_2 + 2\ CaCO_3 \rightarrow 2\ CaCuSi_4O_{10} + 3\ CO_2 + H_2O$

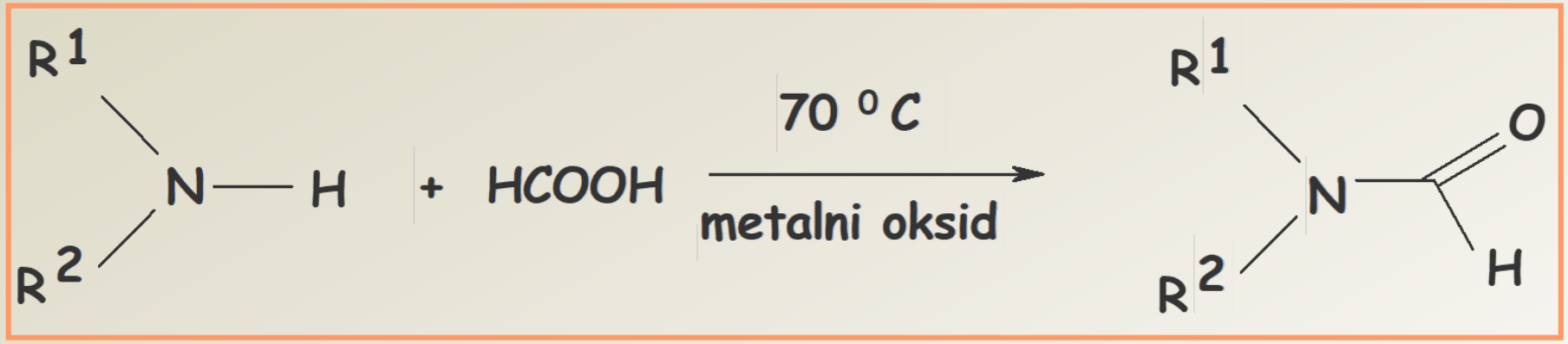
EGIPATSKO PLAVO – PRVI SINTETSKI PIGMENT (Četvrta dinastija, *ca*. 2575.–2467. pr. Kr.)



Vanadís (Freja), J. Bauer, 1905.

SPOJEVI PRIJELAZNIH METALA KAO INDUSTRIJSKI KATALIZATORI

Metalni oksidi: CuO, CoO, NiO, Mn_2O_3, Cr_2O_3



A I BIOLOŠKI KATALIZATORI

DOBIVANJE NH_3

industrijski → $N_2 + 3H_2 \rightarrow 2NH_3$ (uz katalizator, P = 200 atm, t = 400 °C)

biološki → $N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$

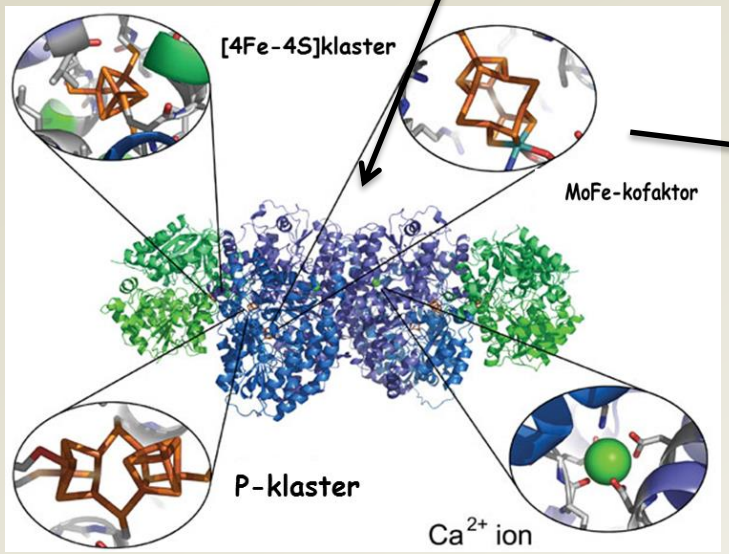
Nitrogenaza: 2 metaloproteina: Fe-protein (hidroliza ATP i prijenos e^- *)*

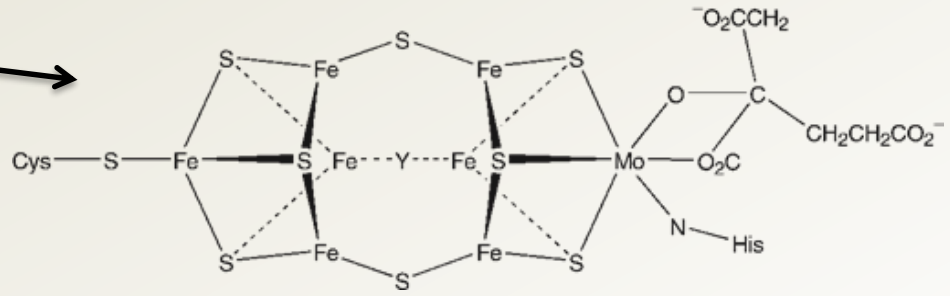
FeMo protein odgovoran za vezanje N_2

Čvorići na korjenu leguminoze

1. Redukcija Fe proteina;
2. Prijenos e^- s Fe proteina na FeMo protein i hidroliza ATP
3. Prijenos e^- i H^+ na N_2

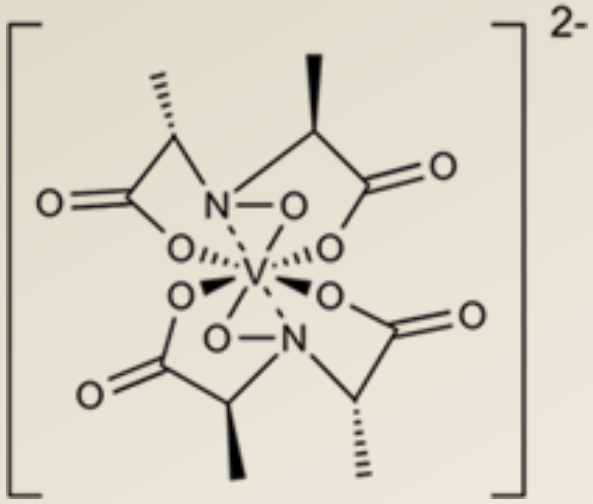
$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16PO_3(OH)^{2-}$$

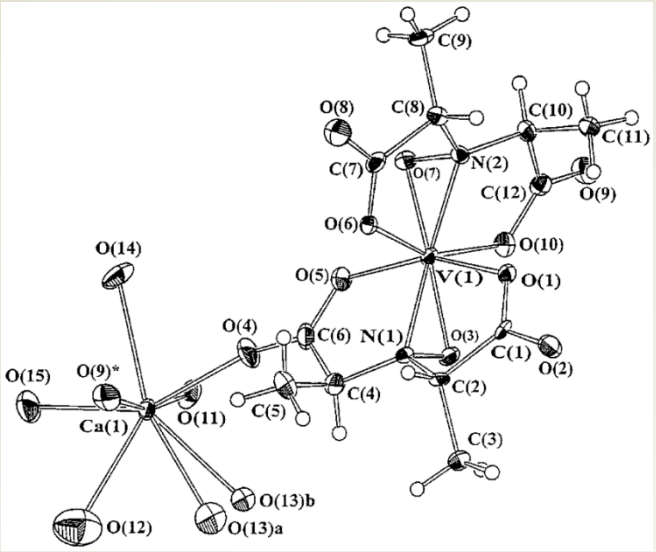




Struktura kompleksa koji nastaje između Fe proteina i MoFe proteina (MoFe-kofaktor) u enzimu nitrogenazi (1992)

SPOJEVI PRIJELAZNIH METALA KAO BILJNI OTROVI (?)





Amavadin, izoliran 1972.

$+ VO^{2+} \rightarrow [V\{NO[CH(CH_3)CO_2]_2\}_2]^{2-} + H_2O + 4H^+$

KAO SUDIONICI U PROCESU PRIJENOSA KISIKA


Bela Lugosi


Riftia pachyptila


Cancer productus

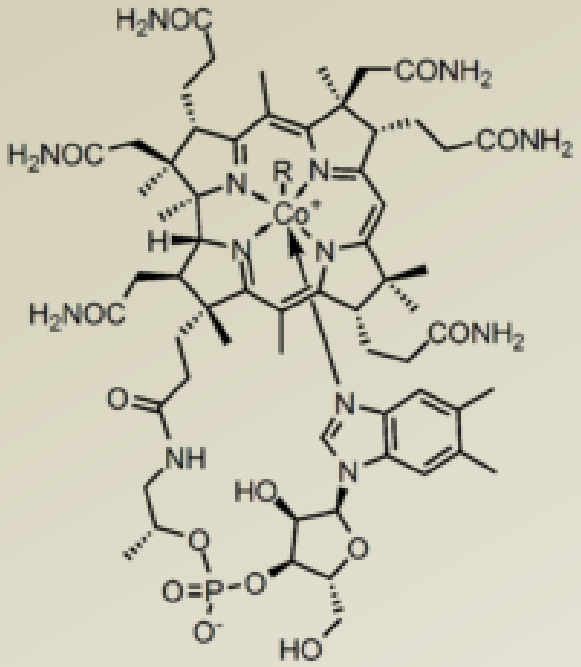

Didemnum molle

Hemoglobin, mioglobin – Fe^{2+}/Fe^{3+}

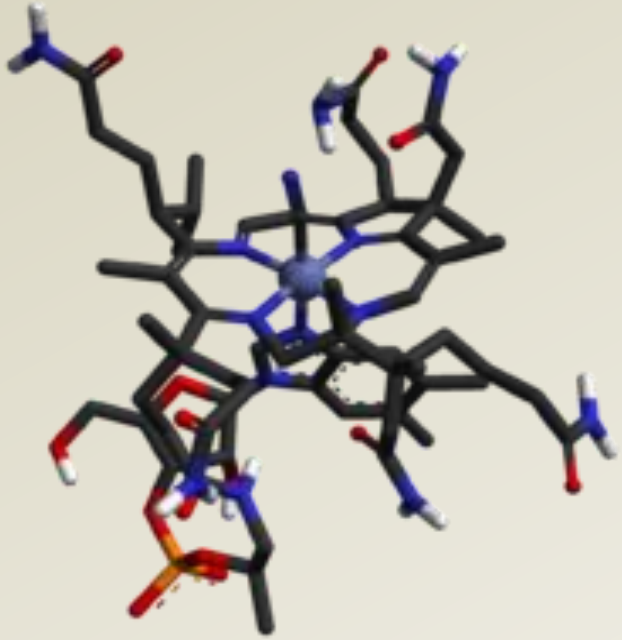
Hemocijanin – Cu^{+}/Cu^{2+}

Hemovanabin – V^{3+}/V^{5+} (funkcija ?)

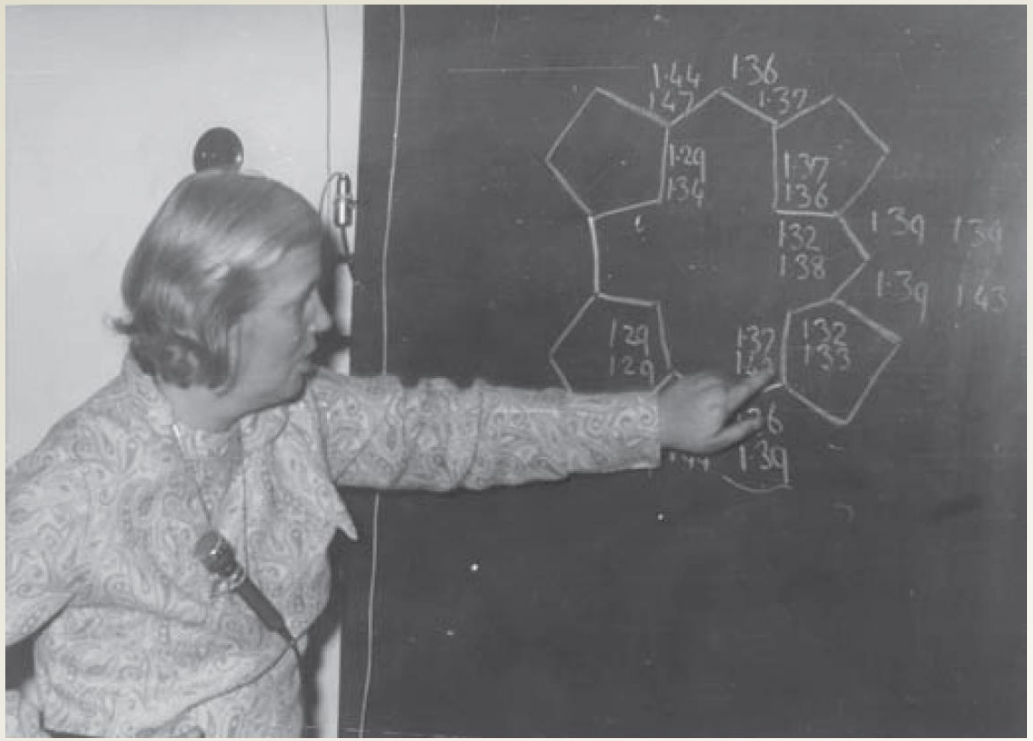
KAO VITAMINI



R = 5'-deoxyadenosyl, Me, OH, CN



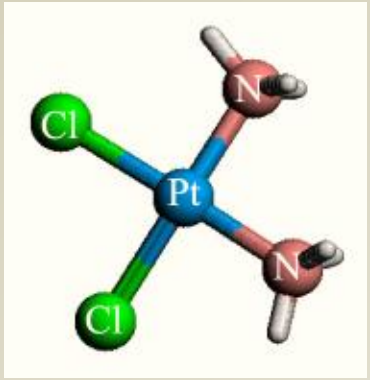
B_{12} – kobalamin



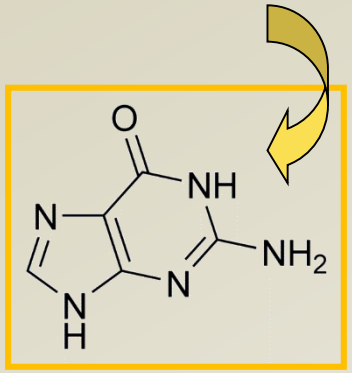
D. Hodgkin (N. n. za kemiju 1964.) na ZOAK-u 1966.

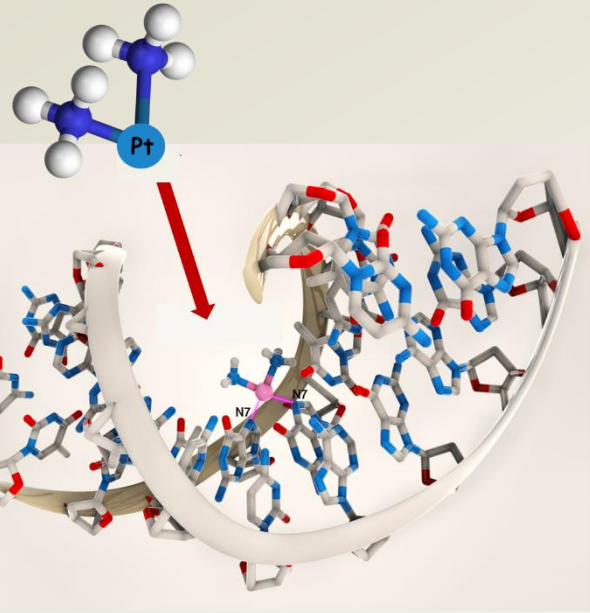
LIJEKOVI

Cisplatin – citostatik poznat od 1960: protutumorsko djelovanje se zasniva na vezanju Pt(II) na gvanin

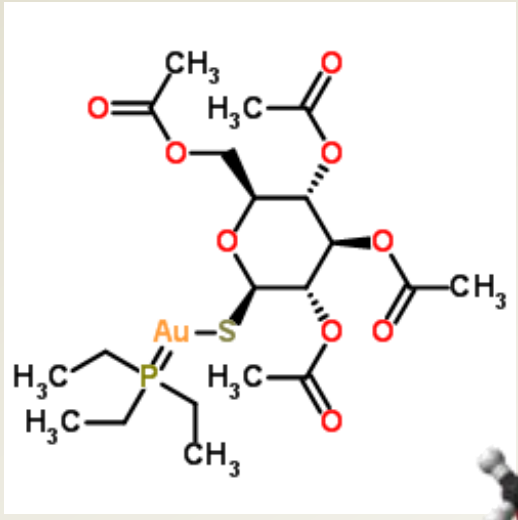


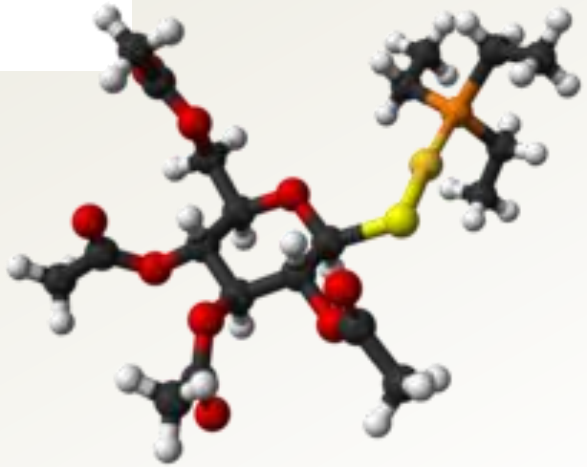
cis-$[PtCl_2(NH_3)_2]$





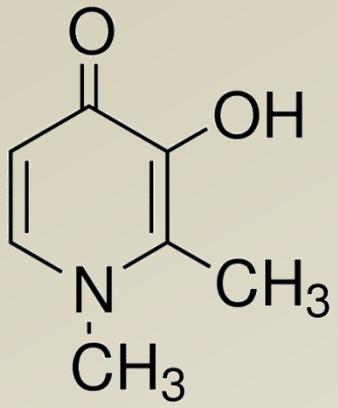
Auranofin – antireumatik, antibiotik i antivirusni agens

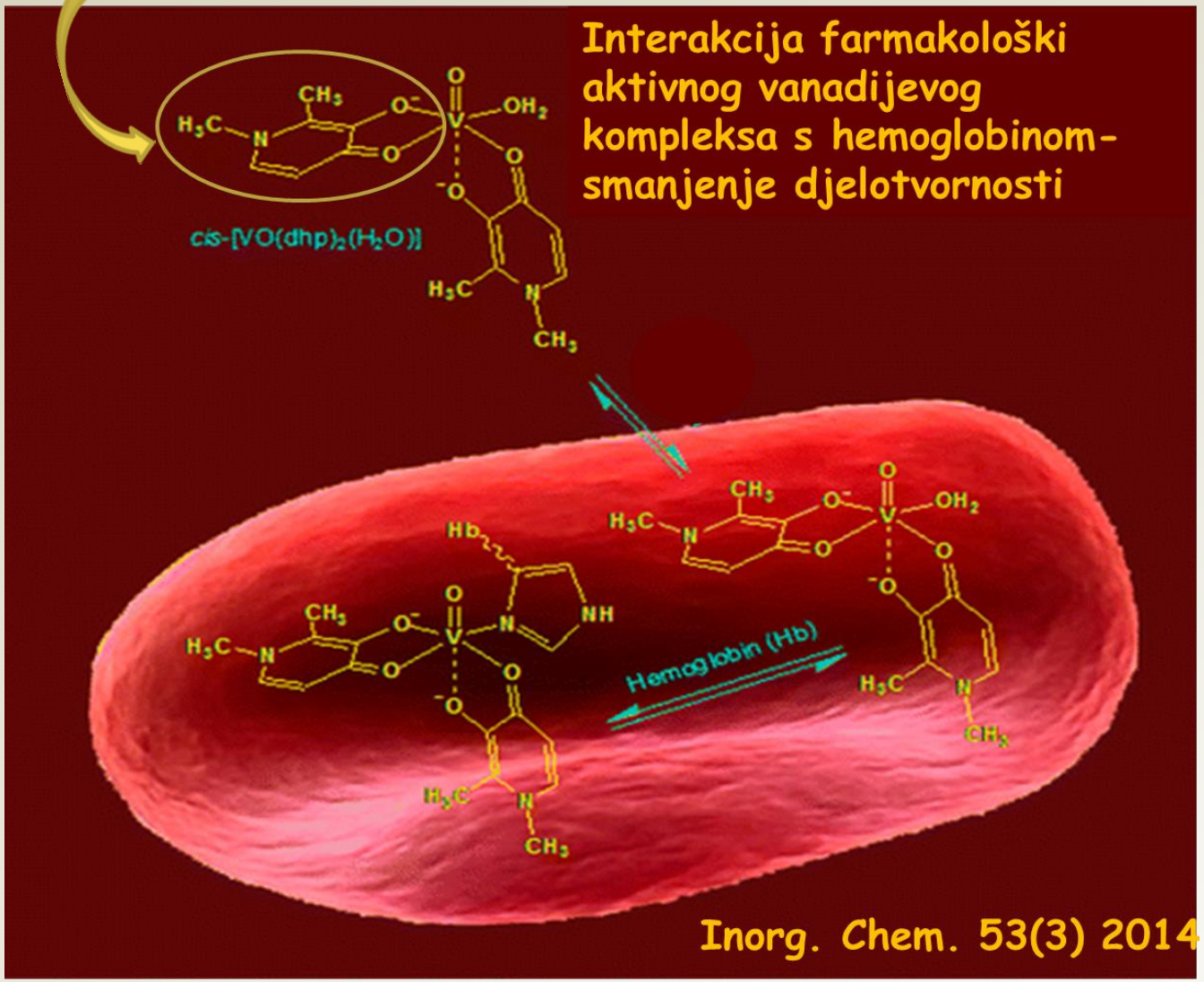


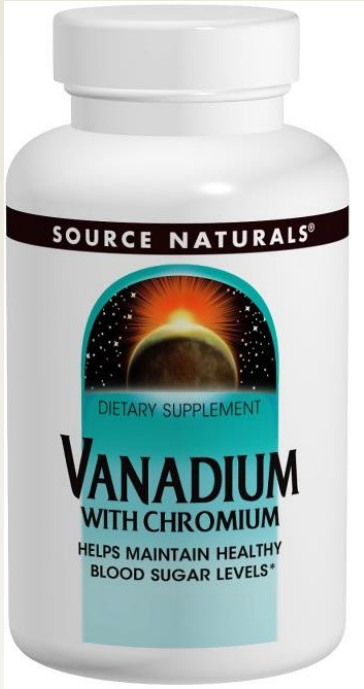


POTENCIJALNI LIJEKOVI

3-hidroksi-1,2-dimetil-4(1*H*)-piridon

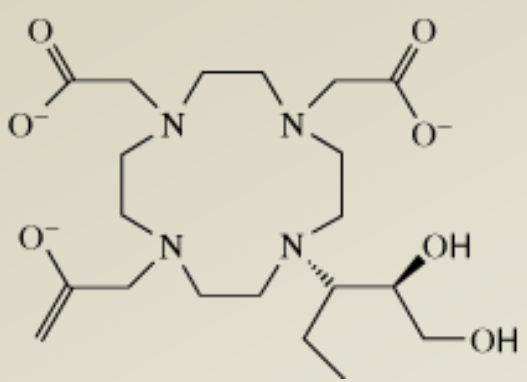


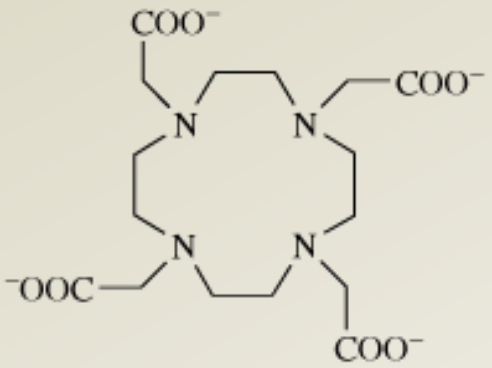


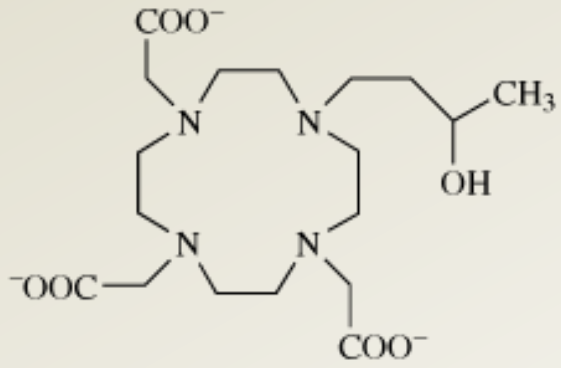


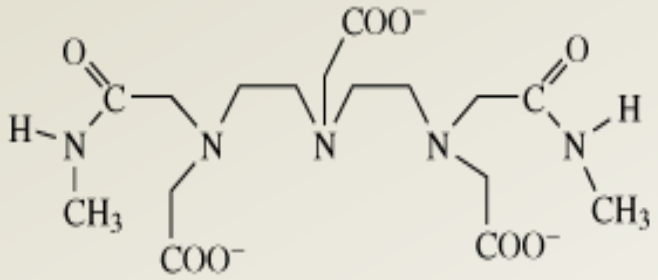
OBILJEŽIVAČI KOD MRI DIJAGNOSTIKE

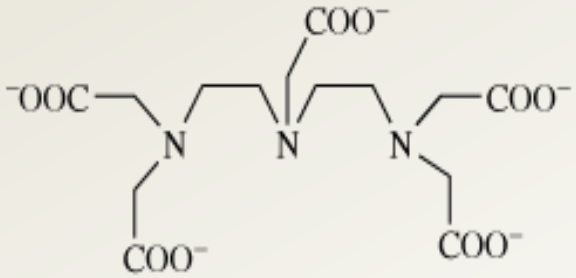
kompleksi Gd^{3+} s organskim ligandima





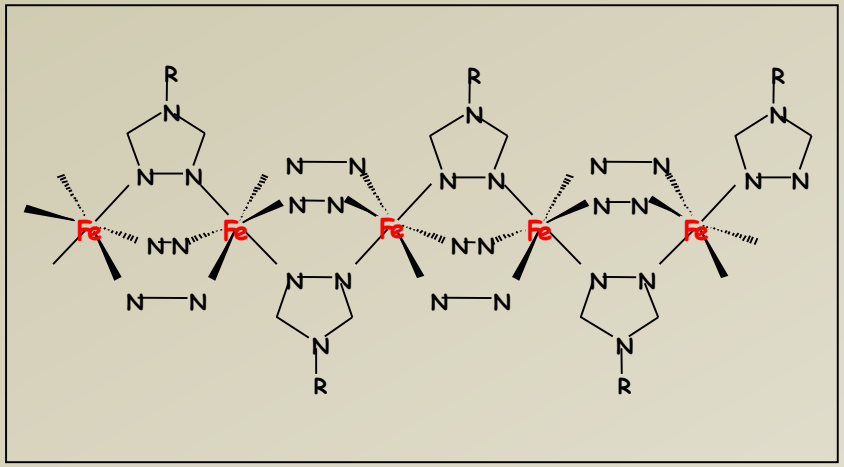


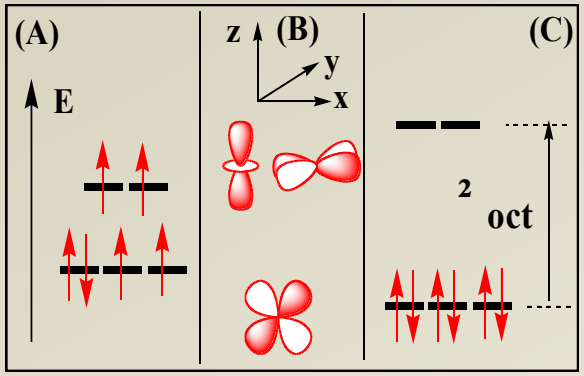


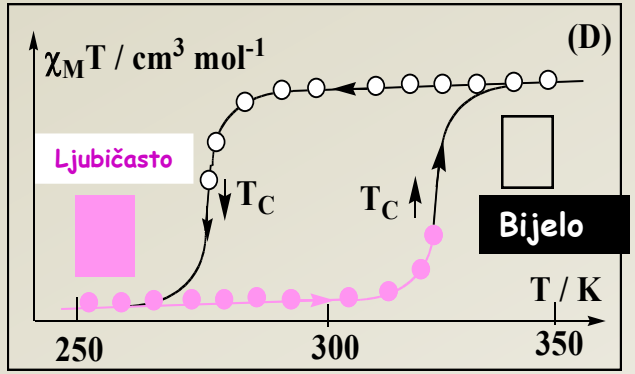


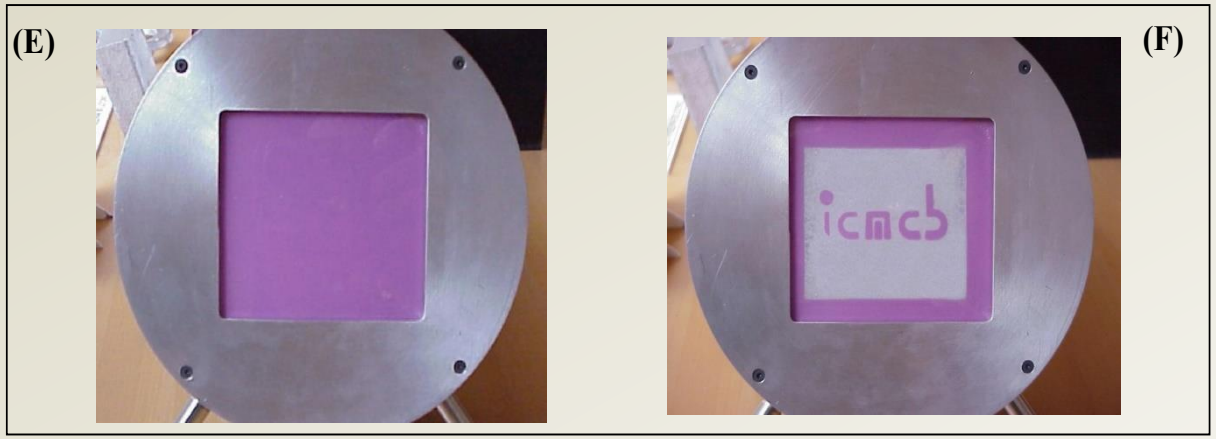
Gd: [Xe] $4f^7\ 5d^1\ 6s^2$; Gd^{3+}: [Xe] $\mathbf{4f^7}$

SENZORI

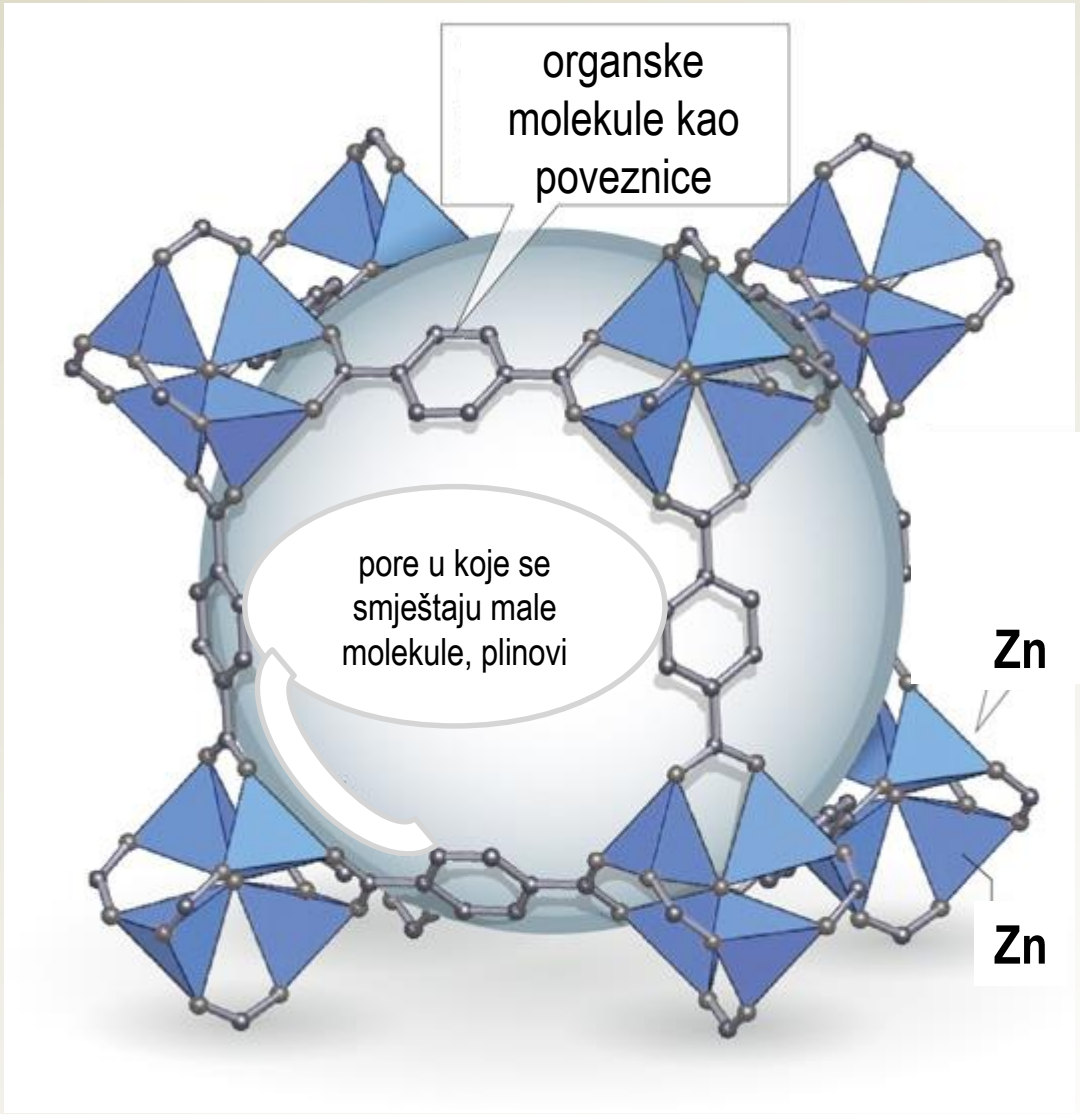








POHRANA PLINOVA

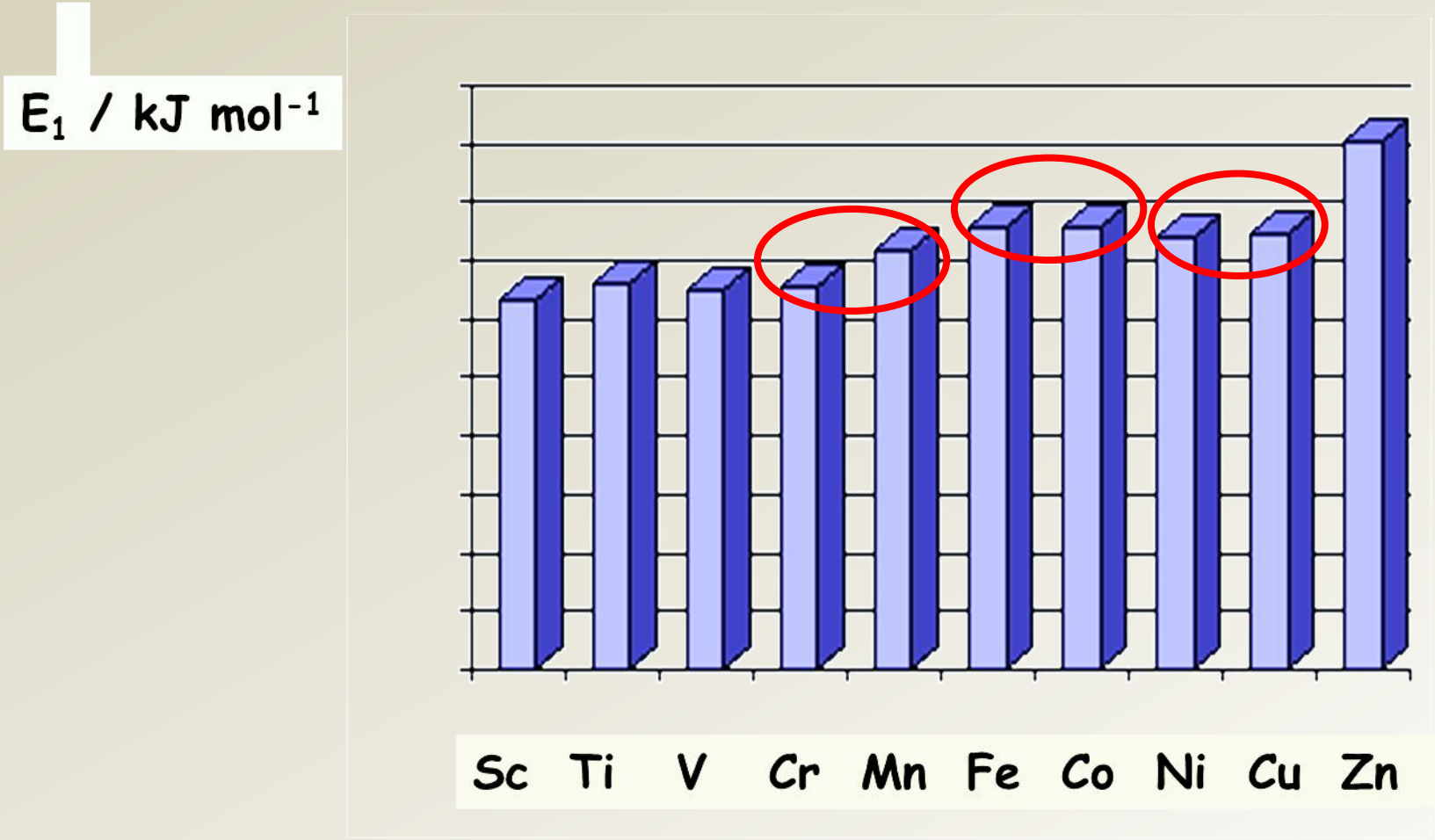


SVOJSTVA PRIJELAZNIH METALA

- Osim nekoliko iznimaka jednostavne (hidratizirane) ione prijelaznih elemenata nalazimo uglavnom u 1. prijelaznoj seriji
- Lantanoidna kontrakcija – smanjenje ionskih i metalnih radijusa
- Energija orbitala 3d niža od energije orbitala 4s: spektroskopska, magnetska mjerenja, teorijska (računski)
- Prilikom ionizacije atoma 1. prijelazne serije najprije se uklanjaju 4s elektroni
- *Anomalije* popunjavanja orbitala d i f kod 21 elementa: složenost elektronskih interakcija

1. PRIJELAZNA SERIJA $[Ar](3d)^n(4s)^n$		2. PRIJELAZNA SERIJA $[Kr](4d)^n(5s)^n$		3. PRIJELAZNA SERIJA $[Xe](5d)^n(6s)^n$	
3. Sc	$(3d)^1(4s)^2$	3. Y	$4d^15s^2$	3. La	$5d^16s^2$
4. Ti	$3d^24s^2$	4. Zr	$4d^25s^2$	4. Hf	$4f^{14}5d^26s^2$
5. V	$3d^34s^2$	5. Nb	$4d^45s^1$	5. Ta	$4f^{14}5d^36s^2$
6. Cr	$3d^54s^1$	6. Mo	$4d^55s^1$	6. W	$4f^{14}5d^46s^2$
7. Mn	$3d^54s^2$	7. Tc	$4d^65s^1$	7. Re	$4f^{14}5d^56s^2$
8. Fe	$3d^64s^2$	8. Ru	$4d^75s^1$	8. Os	$4f^{14}5d^66s^2$
9. Co	$3d^74s^2$	9. Rh	$4d^84s^1$	9. Ir	$4f^{14}5d^76s^2$
10. Ni	$3d^84s^2$	10. Pd	$4d^{10}5s^0$	10. Pt	$4f^{14}5d^96s^1$
11. Cu	$3d^{10}4s^1$	11. Ag	$4d^{10}5s^1$	11. Au	$4f^{14}5d^{10}6s^1$
12. Zn	$3d^{10}4s^2$	12. Cd	$4d^{10}5s^2$	12. Hg	$4f^{14}5d^{10}6s^2$

ENERGIJA IONIZACIJE ELEMENATA 1. PRIJELAZNE SERIJE

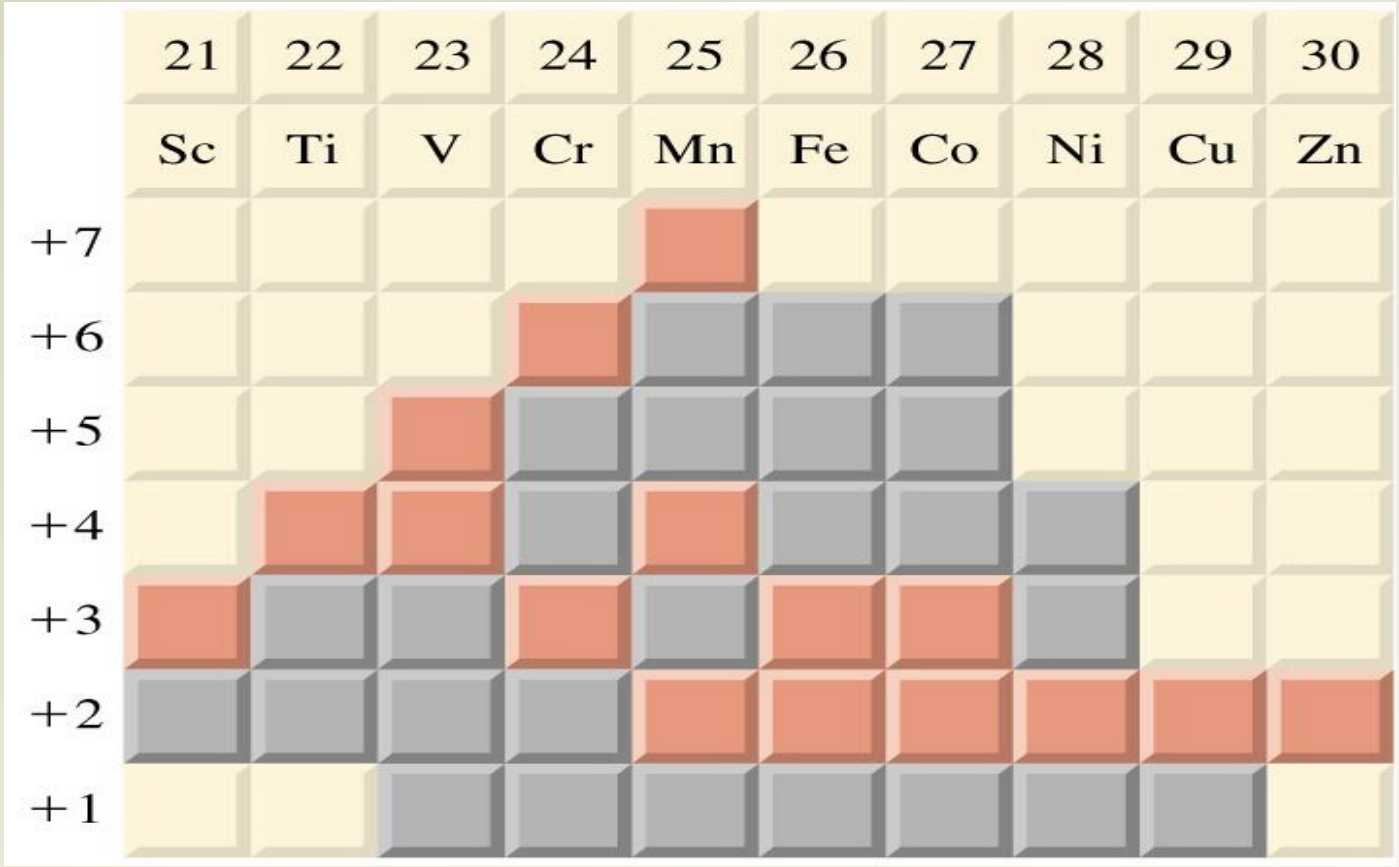


STANDARDNI REDUKCIJSKI POTENCIJAL METALA 4. PERIODE;

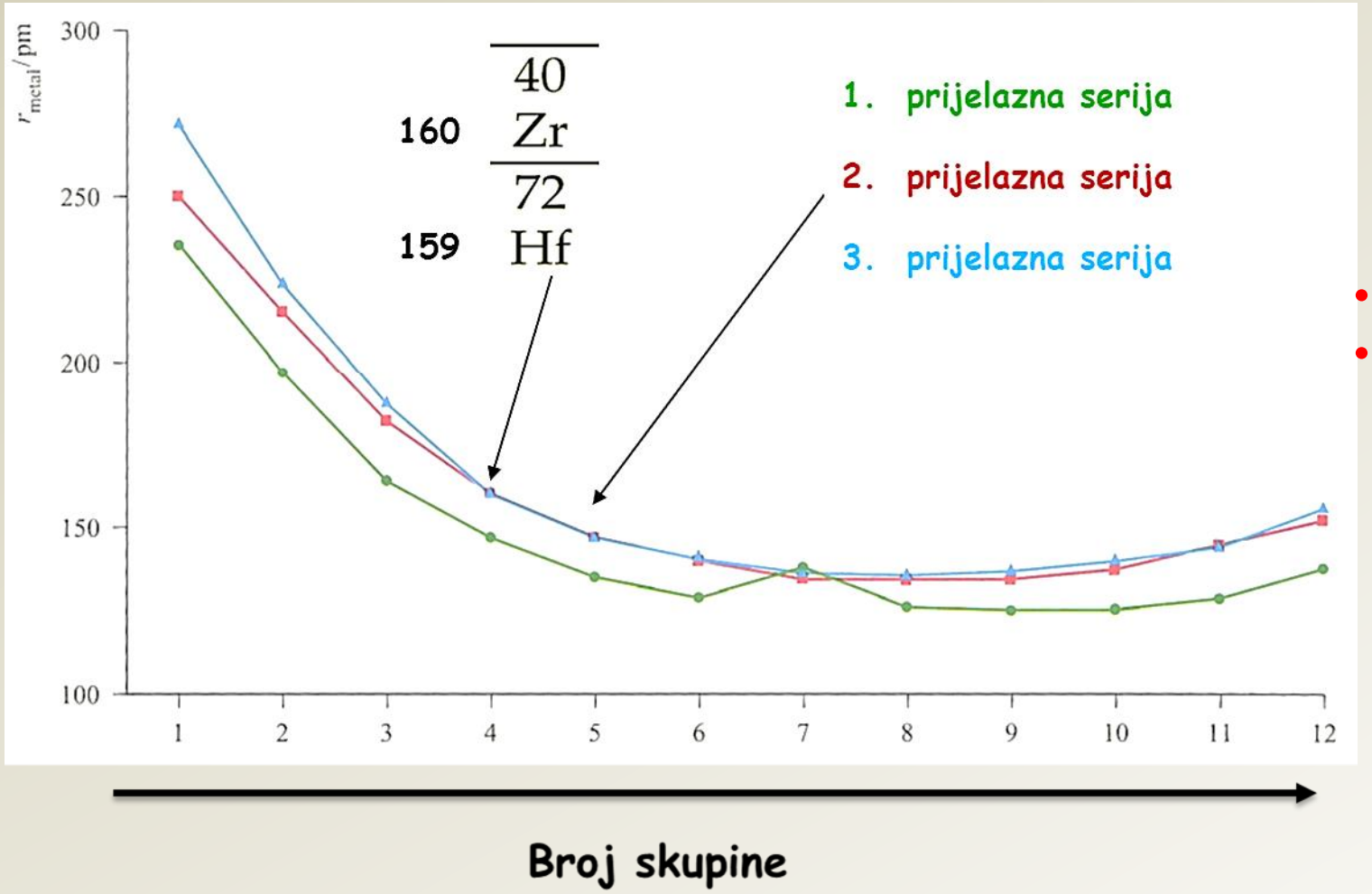
(koncentracija 1 mol dm^{-3}, T = 298 K)

	$E°$ / V
$Ca^{2+}(aq) + 2e^- = Ca(s)$	-2,87
$Ti^{2+}(aq) + 2e^- = Ti(s)$	-1,63
$V^{2+}(aq) + 2e^- = V(s)$	-1,18
$Cr^{2+}(aq) + 2e^- = Cr(s)$	-0,91
$Mn^{2+}(aq) + 2e^- = Mn(s)$	-1,19
$Fe^{2+}(aq) + 2e^- = Fe(s)$	-0,44
$Co^{2+}(aq) + 2e^- = Co(s)$	-0,28
$Ni^{2+}(aq) + 2e^- = Ni(s)$	-0,25
$Cu^{2+}(aq) + 2e^- = Cu(s)$	+0,34
$Zn^{2+}(aq) + 2e^- = Zn(s)$	-0,76

RASPON OKSIDACIJSKIH STANJA ELEMENATA 1. PRIJELAZNE SERIJE



VELIČINA ATOMA ELEMENATA d-BLOKA



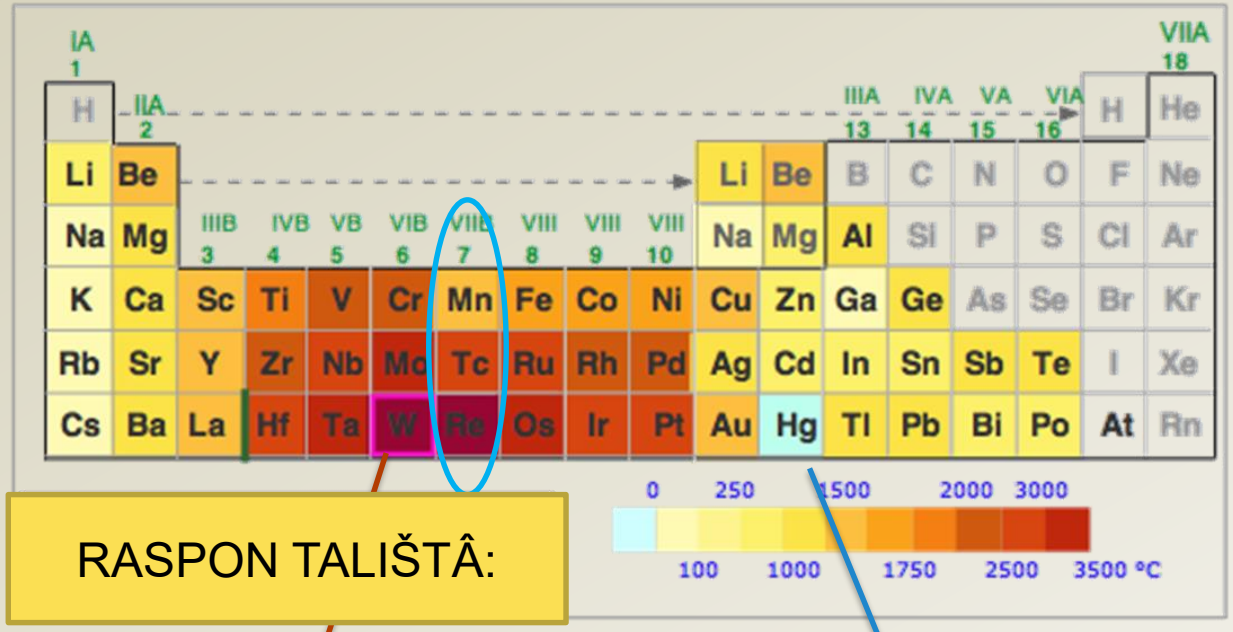
Metalni radijus

- u skupini prema dolje raste
- duž periode se smanjuje

SVOJSTVA (PRIJELAZNIH) METALA:

1. Visoka tališta i vrelišta

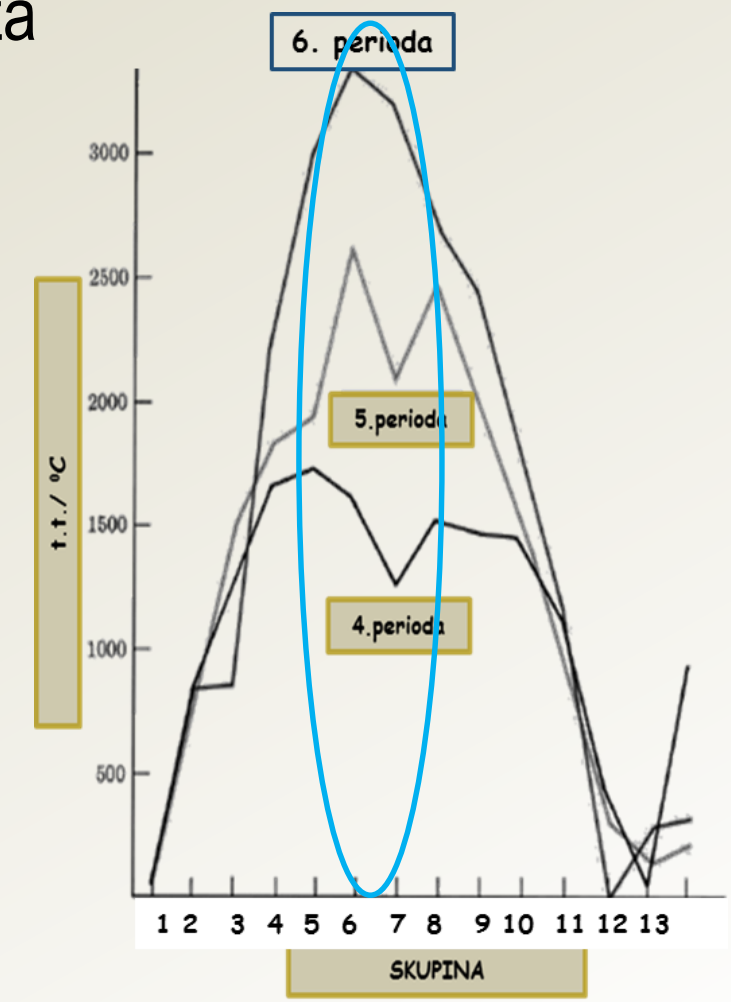
Više talište / vrelište / $\Delta_{fus}H$ / $\Delta_{vap}H$ $\Rightarrow$ jača metalna veza



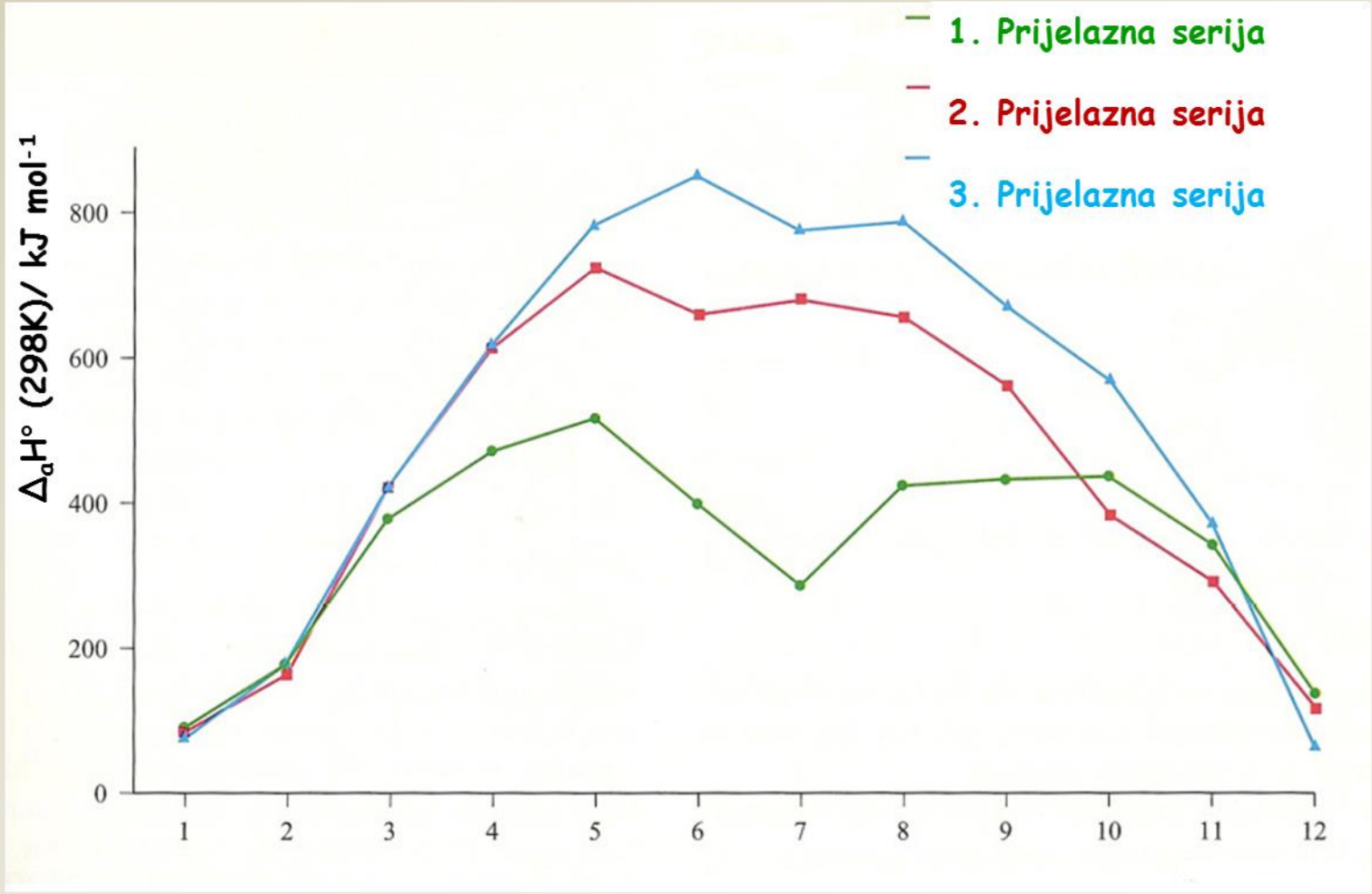
RASPON TALIŠTÂ:

3410 °C
$4f^{14}5d^{4}6s^{2}$

-38,87 °C
$4f^{14}5d^{10}6s^{2}$



STANDARDNA ENTALPIJA ATOMIZACIJE $\Delta_{sub}H°$

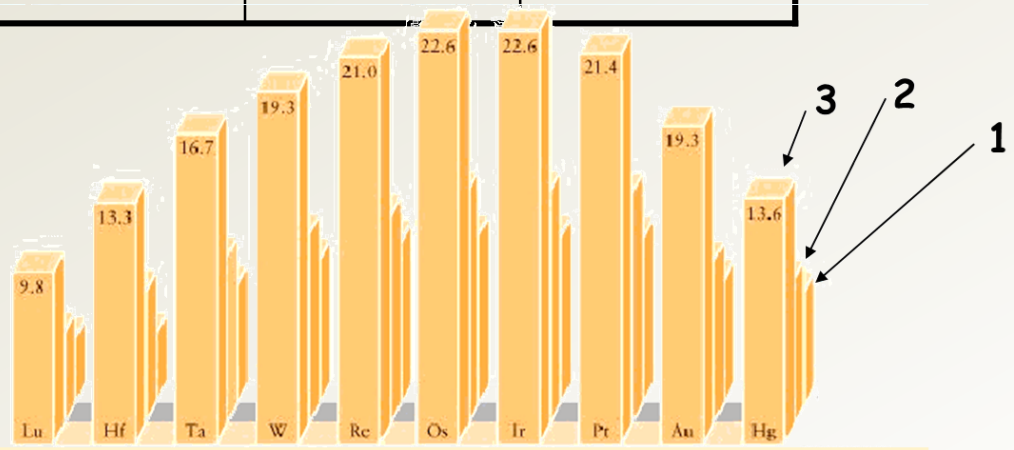


2. Visoka gustoća*

gusta kubična slagalina /gusta heksagonska slagalina koordinacijski broj = 12

Metal	Ni	Cu	Ag	Pb	Hg	Au
Gustoća /g cm^{-3}	8,91	8,94	10,49	10,66	13,53	19,30

* Izuzetak su alkalijski metali; veliki radijusi



Velika gustoća 3. prijelazne serije posljedica → *lantanoidna kontrakcija*

3. Velika fleksibilnost

Kovnost:
Sposobnost deformacije uslijed **kompresije**

(a) Prisutnost slojeva u kristalnoj rešetci
na pr. slojevi mogu kliziti jedan iznad drugog pod pritiskom

Rastezljivost:
Sposobnost deformacije uslijed **napetosti**

(b) Metalne veze su neusmjerene
na pr. elektroni mogu promijeniti položaj i obnoviti metalnu vezu nakon deformacije

METALNA VEZA – TRENDOVI

1. Jakost metalne veze raste sa ***smanjenjem*** radijusa metalnog atoma

metal	radijus / nm	T_t / °C
Cink	0,133	419
Kadmij	0,149	320
Živa	0,150	-38,8

2. Jakost metalne veze raste s **porastom** broja valentnih elektrona metalnog atoma,

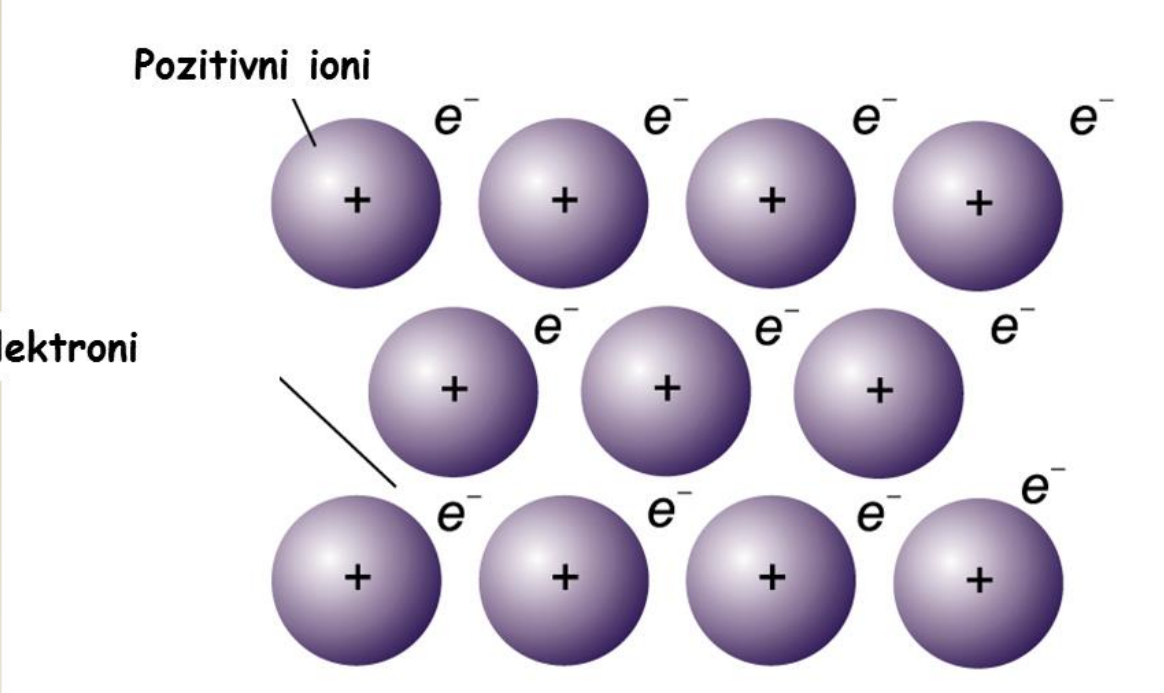
metal	broj valentnih elektrona	T_t / °C
Skandij	3	1539
Titanij	4	1660
Vanadij	5	1890

3. ali samo do koniguracije (ugrubo) d^5 – nakon toga počinje opadati

METALNA VEZA – elektronski model: delokalizacija valentnih elektrona

Metali ne pokazuju tendenciju stvaranja diskretnih molekula (na pr. Li_2) – male energije ionizacije

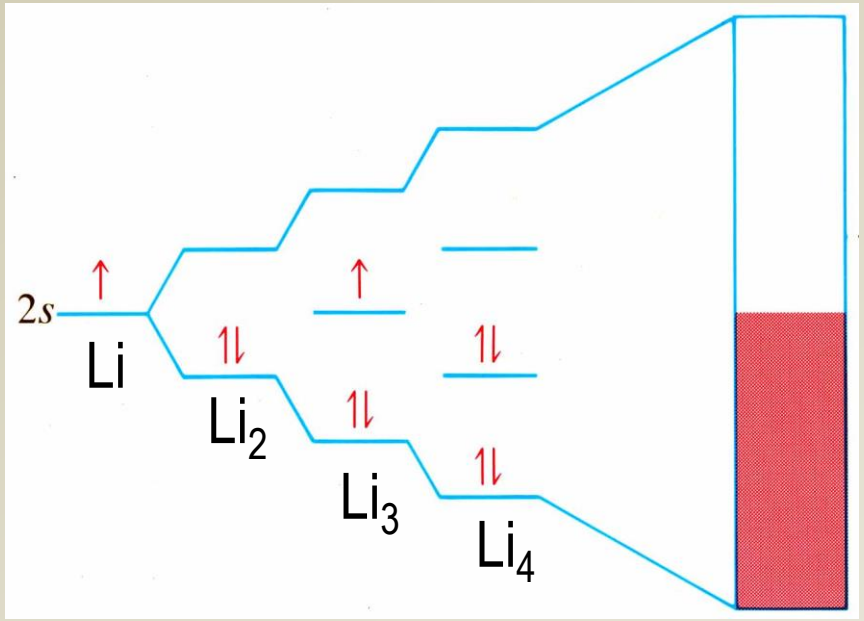
U čvrstom stanju u pravilu gusto pakiranje (neusmjerenost veze, mali broj elektrona u svakom međuatomskom kontaktu)

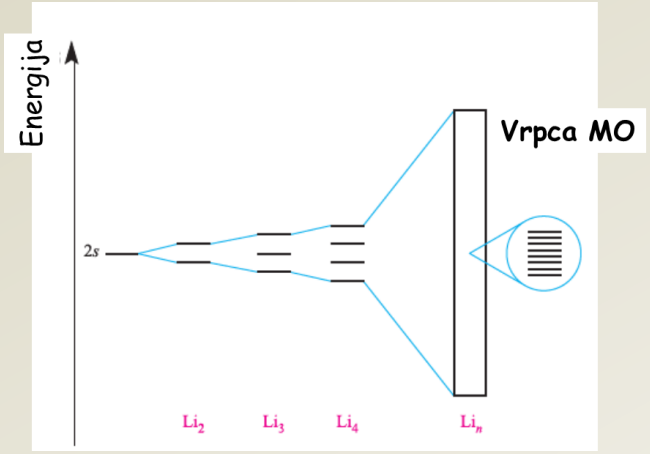


Model delokaliziranih elektrona:

- valentni elektroni nisu lokalizirani već su delokalizirani kroz čitavu strukturu; elektroni mobilni, a pozitivni ioni stacionarni
- elektrostatske privlačne sile delokaliziranog elektronskog oblaka i pozitivnih iona = metalne veze

Model molekulskih orbitala – ‘teorija vrpci’

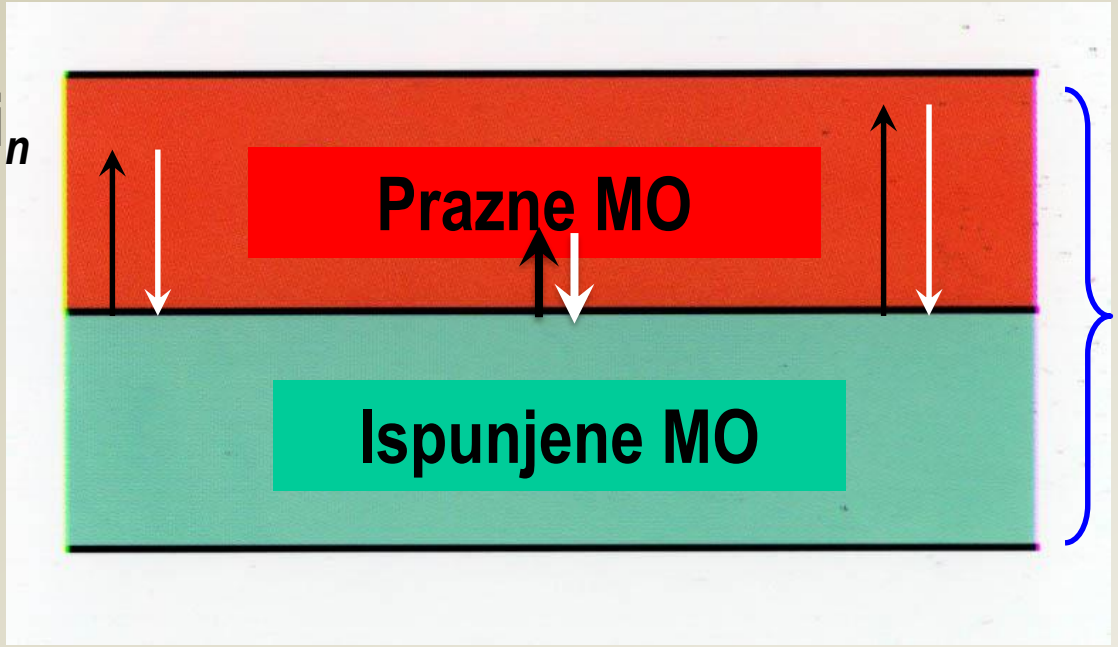




Molekulsko-orbitalni model:

- Cijeli kristal metala tretira se kao jedna molekula
- Energijska stanja opisana molekulskim orbitalama koje obuhvaćaju cijeli kristal
- Zbog makroskopskih dimenzija kristala, razlike energije energijska stanje su *nemjerljivo* bliska – **kontinuum**.
- Energijska stanja iznad energija odgovarajućih (‘ishodnih’) stanja slobodnog atoma su protuvezna, ona ispod su vezna – metalna veza to jača što je veža razlika populacija veznih i protuveznih stanja.

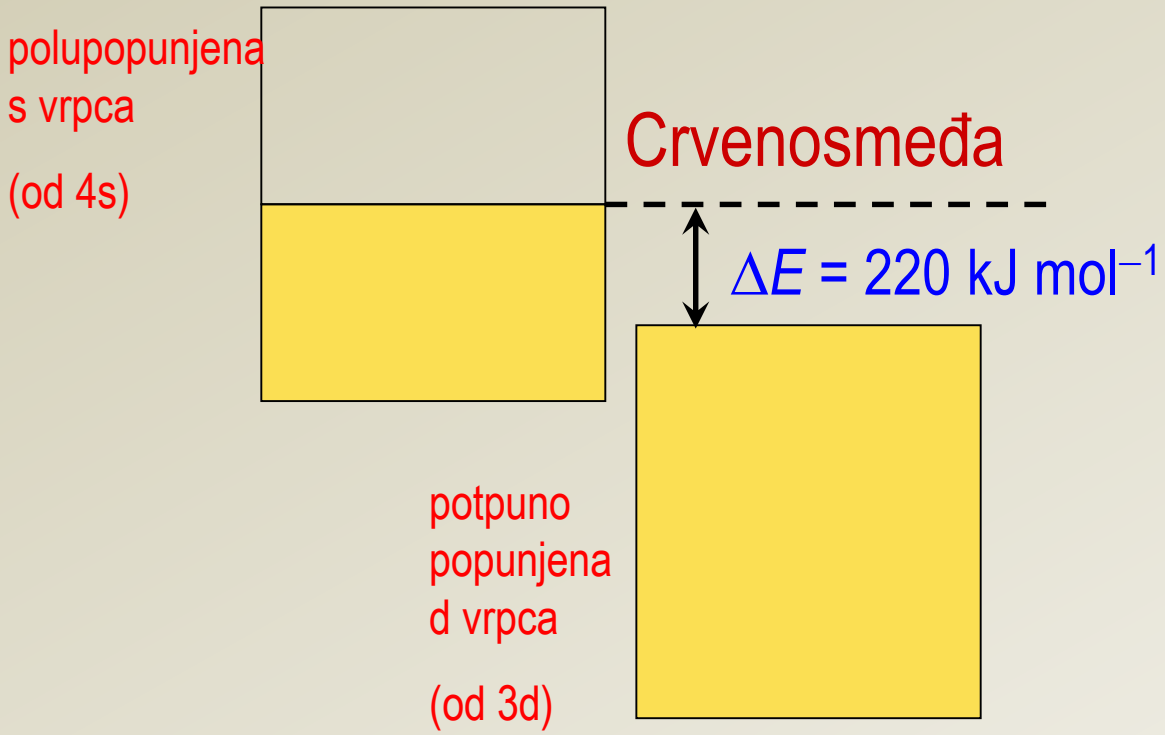
METALNI SJAJ



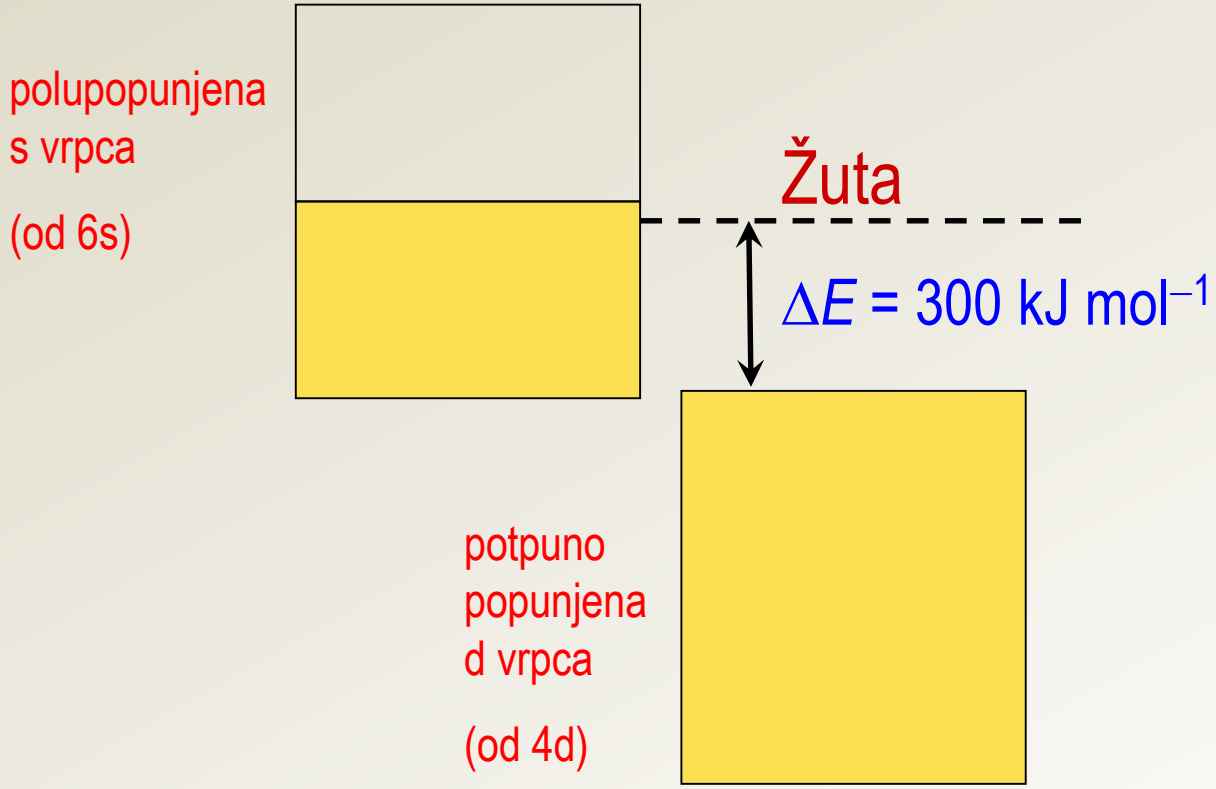
Budući da je razlika između energetskih nivoa ekstremno mala, dolazi do emisije i apsorpcije u vidljivom dijelu spektra – apsorbira se i emitira (u pravilu) cijeli vidljivi spektar

OBOJENI METALI

Cu : $3d^{10}4s^{1}$



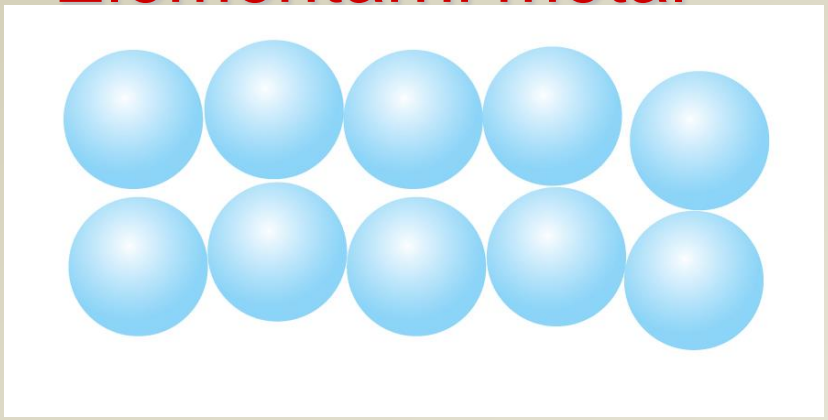
Au : $5d^{10}6s^{1}$



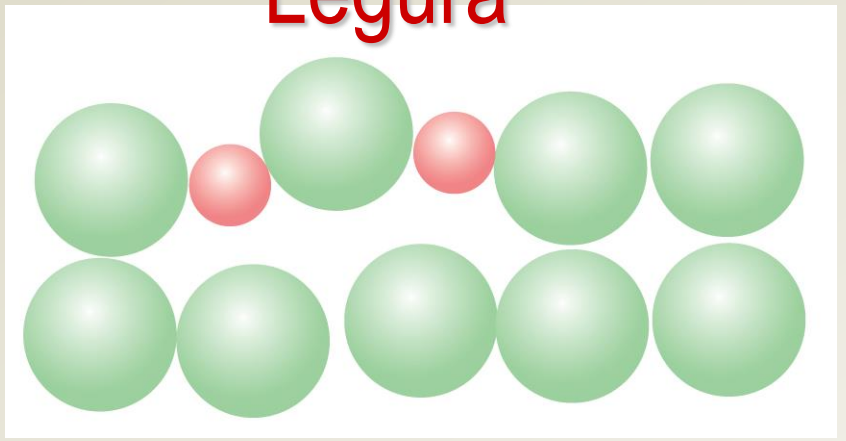
Ukoliko je razlika među energijama popunjene i najnižih nepopunjeh stanja polupopunjene vrpce takva da odgovara energiji kvanta vidljivog zračenja, metal će preferirano apsorbirati dio vidljivog spektra i biti obojan.

LEGURE (SLITINE)

Elementarni metal



Legura



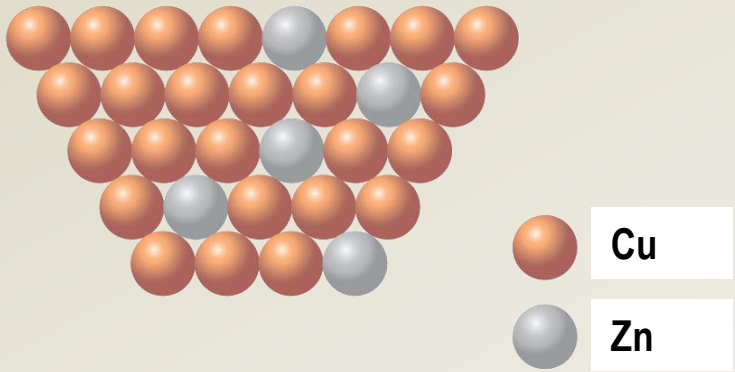
Promjene pravilnog razmještaja slojeva atoma u metalu

Pomicanje slojeva otežano

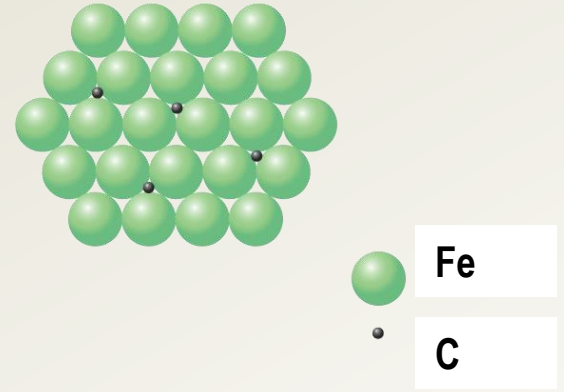
Često čvršće i jače

Tipovi legura

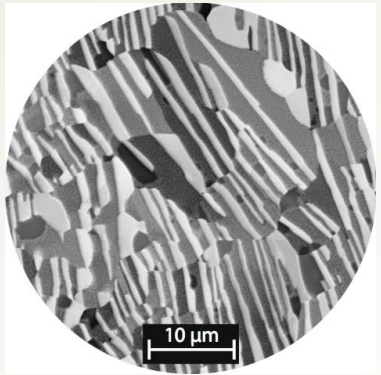
1. Supstitucijske: Kristalna struktura odgovara strukturi jedne komponente, dio atoma zamijenjen atomima drugog metala (atomi sličnih radijusa)



2. Intersticijske: u šupljinama kristalne strukture (među atomima) jedne komponente smješteni atomi druge komponente (atomi manjeg radijusa)



[**3. Eutektičke**: iz homogene taline kristalizira heterogena krutina (zrna pojedinih metala razlučiva golim okom / mikroskopom)]



Ni + Al + Nb

Legure za kovanice

Cu + Sn + Zn

(Fe + C) + Ni

(Fe + C) + (Cu + Sn)

Al + Mg

Cu(75%) + Ni

Cu(92%) + Al + Ni

Nekoć.

Au(90%) + Ag + Cu

Ag(95%) + Cu + Zn

Au(95%)

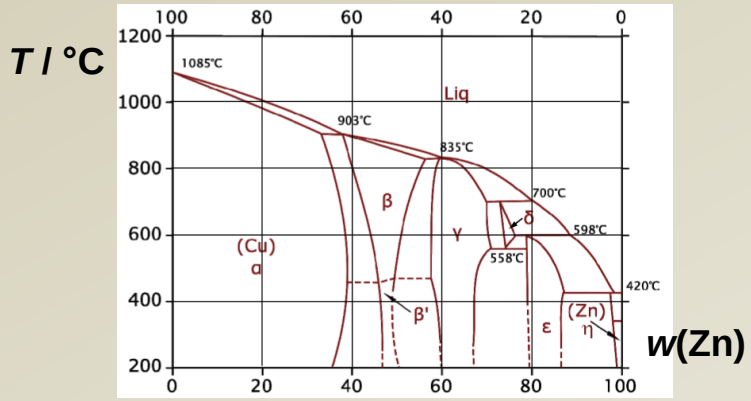
Ag(>97%)

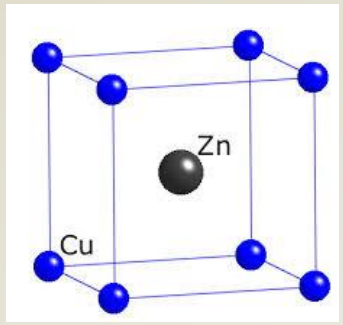
Pt(>90%) + Pd + Ir + ...

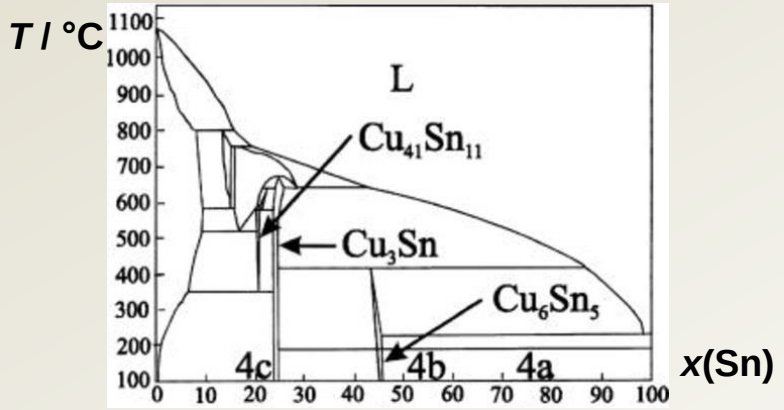
Intermetalni spojevi

Legure (najčešće supstitucijske) koje imaju stalnu stehiometriju (nevarijabilan sastav) i uređenu (periodičnu ili *kvaziperiodičnu*) strukturu.

Uključuju Hume-Rotheryjeve, Lavesove, Frank-Kasperove, Nowotnyjeve, Zintlove (...) faze, ali i neke faze uobičajenih slitina; npr. *žuta* mjed (CuZn), bronce (neke)...







... i **kvaziperiodične** slitine [predpostavljene 1975. (A. L. Mackay), sintetizirane 1982. (D. Shechtman N. n. Za kemiju 2011.)

Pravilne strukture bez periodičke simetrije, binarne i ternarne legure ($Al_{63}Cu_{24}Fe_{13}$, $Al_{71}Ni_{24}Fe_5$...)