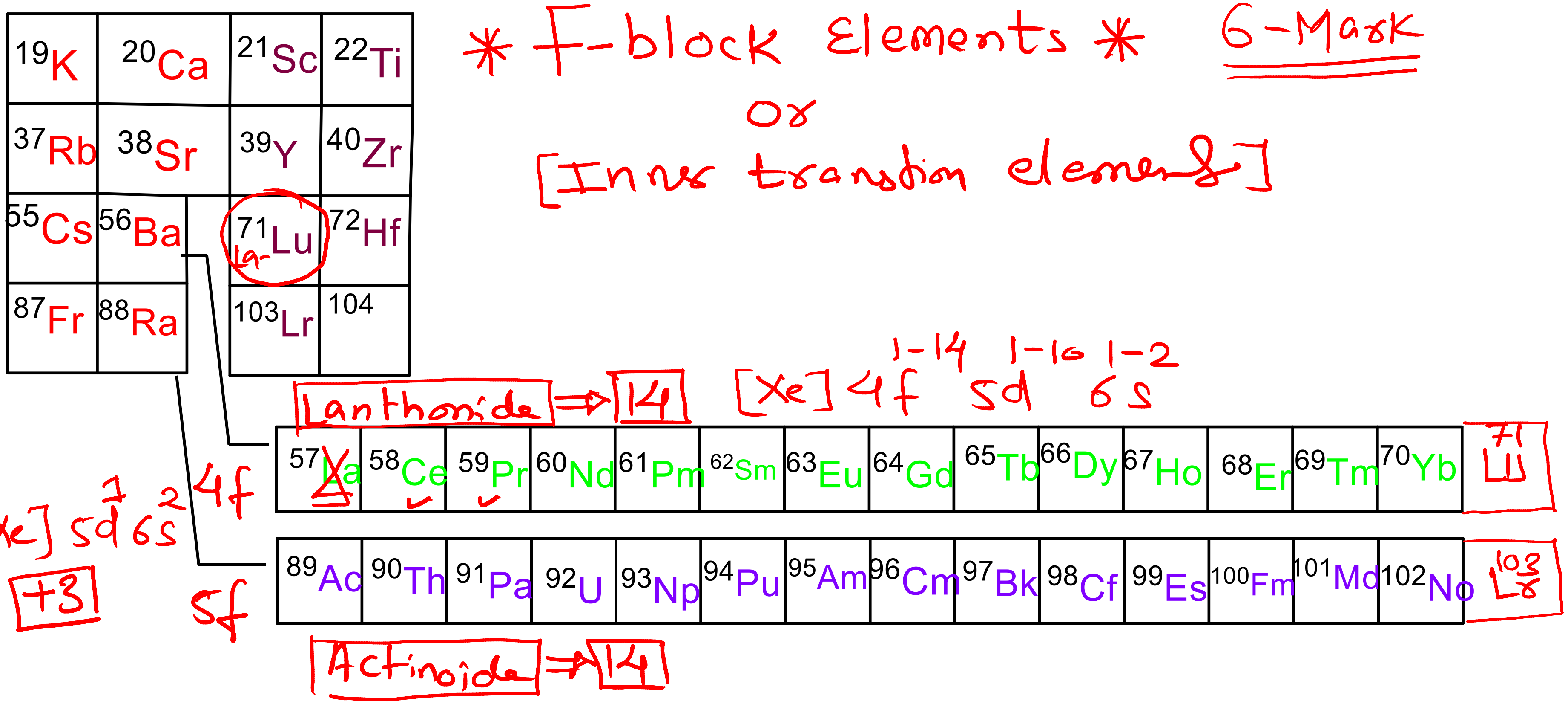
* F-block Elements * 6-Mark

or

[Inner transition elements]



^{19}K	^{20}Ca		^{21}Sc	^{22}Ti
^{37}Rb	^{38}Sr		^{39}Y	^{40}Zr
^{55}Cs	^{56}Ba		^{71}Lu La-	^{72}Hf
^{87}Fr	^{88}Ra		^{103}Lr	104

$\boxed{\text{Lanthanide}} \Rightarrow \boxed{14}$ $[Xe]\,4f^{1-14}\,5d^{1-10}\,6s^{1-2}$

4f

^{57}~~La~~	^{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
^{89}Ac	^{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

5f

$\boxed{\text{Actinoide}} \Rightarrow \boxed{14}$

$La = [Xe]\,5d^{1}\,6s^{2}$

$\boxed{+3}$

Introduction

Lanthanide common oxidn is +3 (Ln^{+3})

Actinoid they show variable oxidn +2, +4, +6, +7

Lanthanoide not act as Radioactive element but
Actinoide act as Radioactive element

General E.C of Ln is $[Xe]\,4f^{1-14}\,5d^{1-10}\,6s^{1-2}$
Ac is $[Rn]\,5f^{1-14}\,6d^{1-10}\,7s^{1-2}$

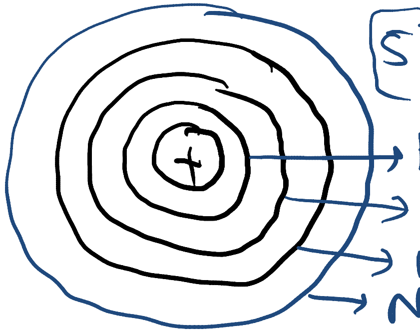
La $\not\Rightarrow$ f-f transition ⇒ Shape

f-Orbitals:

$La \Rightarrow [Xe]_{54}\, \underline{4f^{0}}\; \underline{5d^{1}}\; \underline{6s^{2}}$

$Ce \Rightarrow [Xe]_{54}\, \underline{4f^{1}}\, 5d^{1}\, 6s^{2}$

$[s > p > d > f]$



K ⇒ s $n=0$

L ⇒ s+p $n=1$

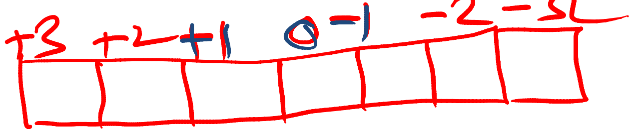
M ⇒ s+p+d $n=2$

N ⇒ s+p+d+f $n=3$

No of Orientation ⇒ $[2l+1]$

$[2\times3+1] = 7$

4f



$n=4$

$l=3$

- * No of Radial node ⇒ $(n-l-1)$
- * No of Angular node ⇒ (l)

Radial node :⇒ $(4-3-1) = 0$

Angular node :⇒ $\boxed{l=3}$

Total Node of 4f

$[n-1]$

$[4-1] = \boxed{3}$

* Electronic configuration:

* $Ln = [Xe]_{54}\, 4f^{1-14}\, 5d^{1-10}\, 6s^{1-2}$

$Ac = [Rn]\, 5f^{1-14}\, 6d^{1-10}\, 7s^{1-2}$

* $f^0,\ f^7,\ f^{14} \Rightarrow$ More stable

$\Downarrow \quad \Downarrow \quad \Downarrow$

$\boxed{\text{Zero filled}}\ \boxed{\text{half filled}}\ \boxed{\text{full filled}} \Rightarrow$ Not show

$\boxed{\Delta S \neq 0}\ \boxed{\Delta S \neq 0}\ \boxed{\Delta S \neq 0}$

[Luminescence Spectra]

[emission Spectra]

$[n+e] = $ $6s = 6+0 = ⑥$ lower Energy
$5d = 5+2 = 7$

Element name	Symbol	Z	Ground state electronic configuration			
			Ln^{0}	Ln^{2+}	Ln^{3+}	Ln^{4+}
Lanthanum	La	57	$[\text{Xe}]6s^{2}5d^{1}$ 54	$[\text{Xe}]5d^{1}\,6s^{0}$	$[\text{Xe}]4f^{0}$	
Cerium	Ce	58	$[\text{Xe}]4f^{1}6s^{2}5d^{1}$	$[\text{Xe}]4f^{2}$	$[\text{Xe}]4f^{1}$	$[\text{Xe}]4f^{0}$
Praseodymium	Pr	59	$[\text{Xe}]4f^{3}6s^{2}$	$[\text{Xe}]4f^{3}$	$[\text{Xe}]4f^{2}$	$[\text{Xe}]4f^{1}$
Neodymium	Nd	60	$[\text{Xe}]4f^{4}6s^{2}$	$[\text{Xe}]4f^{4}$	$[\text{Xe}]4f^{3}$	
Promethium	Pm	61	$[\text{Xe}]4f^{5}6s^{2}$	$[\text{Xe}]4f^{5}$	$[\text{Xe}]4f^{4}$	
Samarium	Sm	62	$[\text{Xe}]4f^{6}6s^{2}$	$[\text{Xe}]4f^{6}$	$[\text{Xe}]4f^{5}$	
Europium	Eu	63	$[\text{Xe}]4f^{7}6s^{2}$	$\boxed{[\text{Xe}]4f^{7}}$ Stable	$[\text{Xe}]4f^{6}$	
Gadolinium	Gd	64	$[\text{Xe}]4f^{7}6s^{2}5d^{1}$	$[\text{Xe}]4f^{7}5d^{1}$	$[\text{Xe}]4f^{7}$ ⇒ half filled stable	

[electropositive]

Terbium	Tb	65	$[Xe]4f^9 6s^2$	$[Xe]4f^9$	$[Xe]4f^8$	$[Xe]4f^7$
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$	$[Xe]4f^{10}$	$[Xe]4f^9$	$[Xe]4f^8$
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$	$[Xe]4f^{11}$	$[Xe]4f^{10}$	
Erbium	Er	68	$[Xe]4f^{12} 6s^2$	$[Xe]4f^{12}$	$[Xe]4f^{11}$	
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$	$[Xe]4f^{13}$	$[Xe]4f^{12}$	
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$	$\boxed{[Xe]4f^{14}}$ stable	$[Xe]4f^{13}$	
Lutetium	Lu	71	$[Xe]4f^{14} 6s^2 5d^1$	$[Xe]4f^{14} 5d^1$	$[Xe]4f^{14}$ Full filled stable	
			0	$\boxed{+2}$	$+3$	

[all Ln^{+3} elements stable in 3+ o.s]

Eu^{+2}, Yb^{+2} ⇒ stable

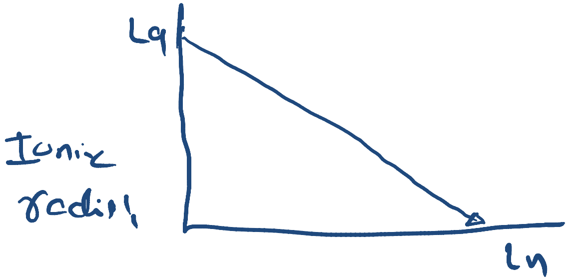
Sm^{+2} Tm^{+2}

Ion sizes and Atom ,metallic radii:

Common O.S +3 (Ln^{+3}) ⇒ [Ionic radii]

If O.S is $\boxed{\text{Zero}}$ (Ln^{0}) ⇒ [Metallic radii]

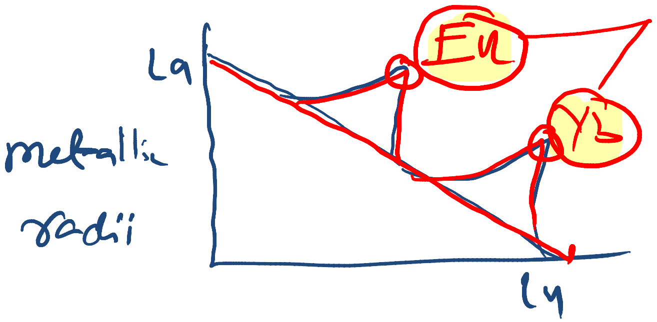
If periodic table left to Righ Ionic radii is ↓



$Eu = [Xe]\,4f^{7}\,6s^{2}\,5d^{0}$

$Yb = [Xe]\,4f^{14}\,6s^{2}\,5d^{0}$

Stable

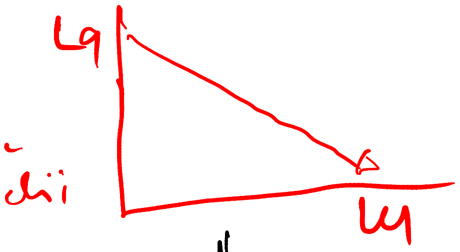


abnormal high metallic radii

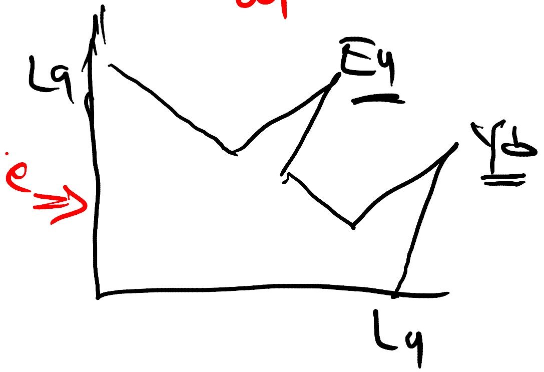
Atom and ion sizes and metallic radii:

Element name	Symbol	Radius / pm Ln	 Ln^{3+}
Lanthanum	La	188	116
Cerium	Ce	183	114
Praseodymium	Pr	182	113
Neodymium	Nd	181	111
Promethium	Pm	181	109
Samarium	Sm	180	108
Europium	Eu half filled	199	107
Gadolinium	Gd	180	105
Terbium	Tb	178	104
Dysprosium	Dy	177	103
Holmium	Ho	176	102
Erbium	Er	175	100
Thulium	Tm	174	99
Ytterbium	Yb Full filled	194	99
	Lu		

Ln^{3+} ⇒ Ionic radii



Metallic radii ⇒



Eu & Yb in zero o.s Show abnormal high metallic radii oxidise ⇒ [Reducing agent]

$Eu^{+2} \rightarrow \boxed{Eu^{+3}}$

* Reduction potential

The standard reduction potentials (E^0) are all high ~~(Table 29.2)~~.
They vary in a regular way over a small range from $\boxed{-2.48}$ to $\boxed{-2.26}$ volts depending on the size of the ions. The lanthanides are all much more reactive than is Al (E^0 = -1.66 volts) and are slightly more reactive than Mg (E^0 = -2.37 volts).
Thus, they react slowly with cold water but more rapidly on heating.

$$Ln + 6H_2O \rightarrow \boxed{2Ln(OH)_3} + 3H_2$$

[Basic nature]

$Ln^{+3} > Al^{+3}$

① Size ↑ Basicity ↑

② [s-block > Ln > p-block]

$[Ln(OH)_3] > [Al(OH)_3]$

more basic

less basic

Basicity of lanthanoide elements

Basicity of hydroxides and oxides

more basic

$[Na(OH)_6]$ $Ln(OH)_3$ $Al(OH)_3$ Less basic

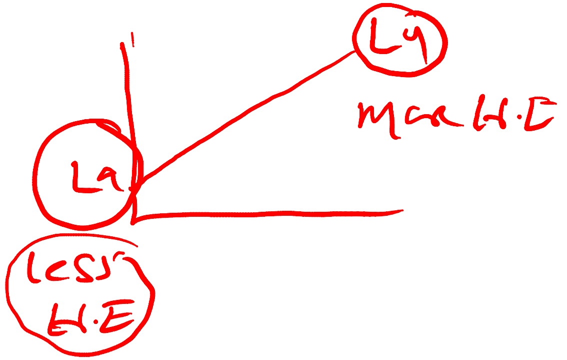
s-block > Ln^{+3} > p-block

Hydration Energy of lanthanoide elements $\propto$ L.E

Hydration energy (also hydration enthalpy) is the amount of energy released when one mole of ions undergo hydration which is a special case of solvation.

[left to righ in La element H.E ↑]

[La → Lu Hydration ↑]



Less H.E

$Na + 6H_2O \rightarrow [Na(OH_2)_6]^+$

max H.E

$Zn + 6H_2O \rightarrow [Zn(OH_2)_6]^{+2}$

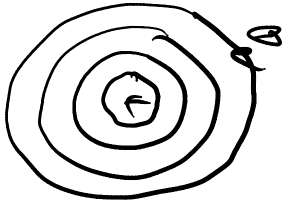
Large size element
Less H.E

Small size element
max H.E

$[H.E \propto L.E]$

$H.E \propto Z_{eff}$

Ionization Energy of Lanthanoide elements



$\xrightarrow{E} IE$

1) Lanthanides have fairly low ionisation energies

$X \xrightarrow{IE_1} X^{+} \xrightarrow{IE_2} X^{++} \xrightarrow{IE_3} X^{+++}$

2) Due to low values of ionisation energies, lanthanides are highly electropositive in nature. The values of standard reduction potential (E values) increase from La to Lu. E^0 values become less negative in the series.

$Eu = 4f^7 6s^2$

$Yb = 4f^{14} 6s^2$

$\Downarrow$

$\boxed{max\ IE_3}$

3) All the lanthanides are, thus, strong reducing agents. The reducing power decreases from La to Lu.

$Eu \xrightarrow{e} Eu^{+1}$

$4f^7 6s^2 \quad 4f^7 6s^1$

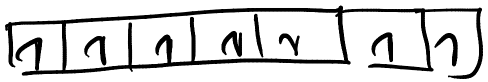
La —— Lu [Reducing power ↓]

* [Common o.s $\boxed{+3}$]

$\leftarrow Eu^{+2}$ $4f^7 6s^0$

$Eu = [Xe]_{54} 4f^7 5d^0 6s^2$

$f^7 =$



Screening effect of lanthanides elements

S-block

$\boxed{n\uparrow \quad \sigma\uparrow}$

$La \longrightarrow Lu$

$Z = 57 \longrightarrow Z = 71$

$Z_{eff}\uparrow \quad \sigma\downarrow$

$(p) \rightarrow 57$ $\qquad (p) \rightarrow 71$

$e = 57$ $\qquad e = 57$

$$\left[Z_{eff} \propto \frac{1}{\text{Screening effect}} \right]$$

[If La element left to right Screening effect decreases & $Z_{eff}\uparrow$]

$\Rightarrow \quad s > p > d > f$

[Less diffused] $\qquad$ [Max diffused]

Penetration of F-orbital less

Partition coefficient of lanthanides elements

Less size max partition coefficient

$Z_{eff} \propto P.C$

$H.E \propto P.C$

[In Ln^{+3} element Left to Right ($La \longrightarrow Lu$) partition coefficient ↑]

Which of the following is max P.C

Ⓐ Ce^{+3} Ⓑ Eu^{+3}

Ⓒ Gd^{+3} ~~ⓓ~~ Yb^{+3}

Yb^{+3} = small size

[High P.C]

Oxidation state of lanthanides elements

\# Common oxidⁿ state of Ln elements is $\boxed{+3}$ #

\# Varible oxidⁿ state of Ln is $\underline{+2}$, $\underline{+4}$, $+3$

$4f^{7}$
$4f^{0}$
$4f^{14}$
} stable

$Eu^{0}\ [Xe]_{54}\ 4f^{7}\ \underline{6s^{2}}\ 5d \longrightarrow \boxed{Eu^{+2}}\ [Xe]_{54}\ 4f^{7}\ 6s^{0}\ 5d^{0}$

stable

$Ce^{0}\ [Xe]_{54}\ 4f^{\textcircled{1}}\ 6s^{\textcircled{2}}\ 5d^{\textcircled{1}} \longrightarrow Ce^{+4}\ [Xe]\ 4f^{0}\ 5d^{0}\ 6s^{0}$

$Z = 58$

\# Eu^{+2}, Yb^{+2}, Sm^{+2}, Tm^{+2} stable in $+2$

\# Ce^{+4} stable in $+4$ oxidⁿ state

The stability of the elements in the different oxidation states givevs the information about the oxidizing power and reducing power of that particular element. This can be illustrated by the followmg three examples:

$\overset{+7}{MnO_4^{\ominus}}$ $d^0 \xrightarrow[e^{\ominus}]{gain\ of} d^1$

1) Ce^{4+} is a strong oxidising reagent:

Electronic configuration of Ce is $4f^1 5d^1 6s^2$. Ce is most stable in +3 state. In +4 state it is most oxidizing because in +4 state it can give an electron to become more stable at +3 state.

CAN (Ceric Ammonium Nitrate) is a stronger reagent than $KMNO_4$ and $K_2Cr_2O_7$ in some reactions.

(+6)(d^0)

[Common O.S]

More stable $Ce^{+4} \xrightarrow[Reduction]{gain\ of\ e^{\ominus}} Ce^{+3}$

(CAN) ↓ [Oxidizing agent]

2) Eu^{2+} is a strong reducing reagent:

Eu^{2+} is less stable than that of the Eu^{3+} due to configurational reasons as stated in the above table. Thus Eu^{2+} acts as a strong reducing agent.

$Eu(SO_4)$

$(+2)$

Common o.s

$$Eu^{+2} \xrightarrow[\text{oxid}^{n}]{\text{loss of } e^{\ominus}} Eu^{+3}$$

[Reducing agent]

3) Sm^{2+} is a strong oxidising reagent:

$[SmI_2]$

Whereas in Sm^{+2}, the lanthanides are more stable in +3 state and hence in +2 state it gets oxidized easily (good reducing agent) to get to +3 oxidation state.

Oxidation state actinode

Stable = +3 Am, Cm, Bk, Cf, Es, Fm, Md, Lr

+4 , Th, U, Pu,

$\boxed{+5}$ Pa ~~•~~ Np

$\boxed{+2}$ No

Table Oxidation states of actinium and the actinoids. The most stable states are shown in bold.

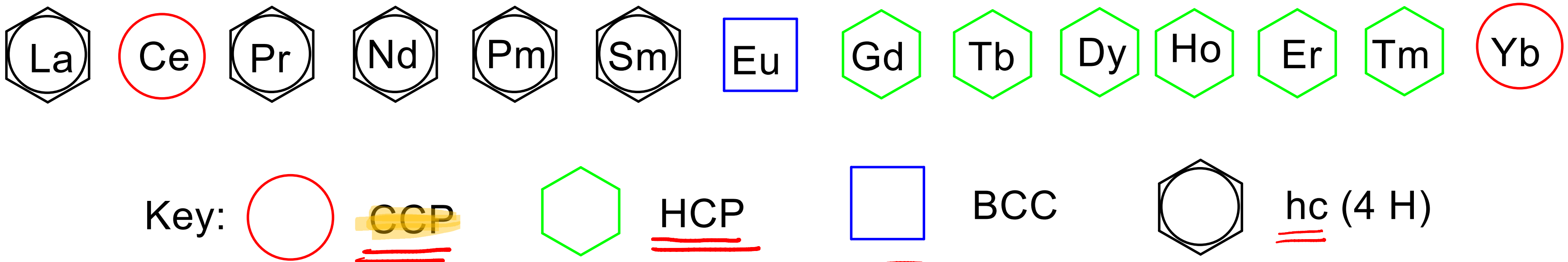
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						2			2	2	2	2	**2**	
3			3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
	4	4	**4**	4	**4**	4	4	4	4					
		5	5	**5**	5	5								
			6	6	6	6								
				7	7									

⇒ (High O.S)

$\left.\begin{matrix}\text{Pa}\\ \text{Np}\end{matrix}\right\}$ +5 ⇒ Stable

$\boxed{\text{Th, U, Pu = +4}}$

Structures of Elemental Metals



Ce
Yb

Gd
Tb
Dy
Ho
Er
Tm

Eu

Sm
Pm
Nd
Pr
La

Lanthanide contraction :

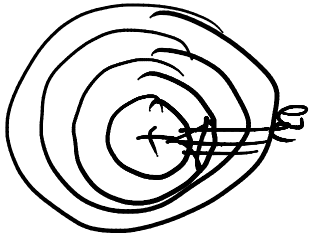
3d Sc Ti V Co Mn

4d Y Zr Nb Mo ~~Tc~~

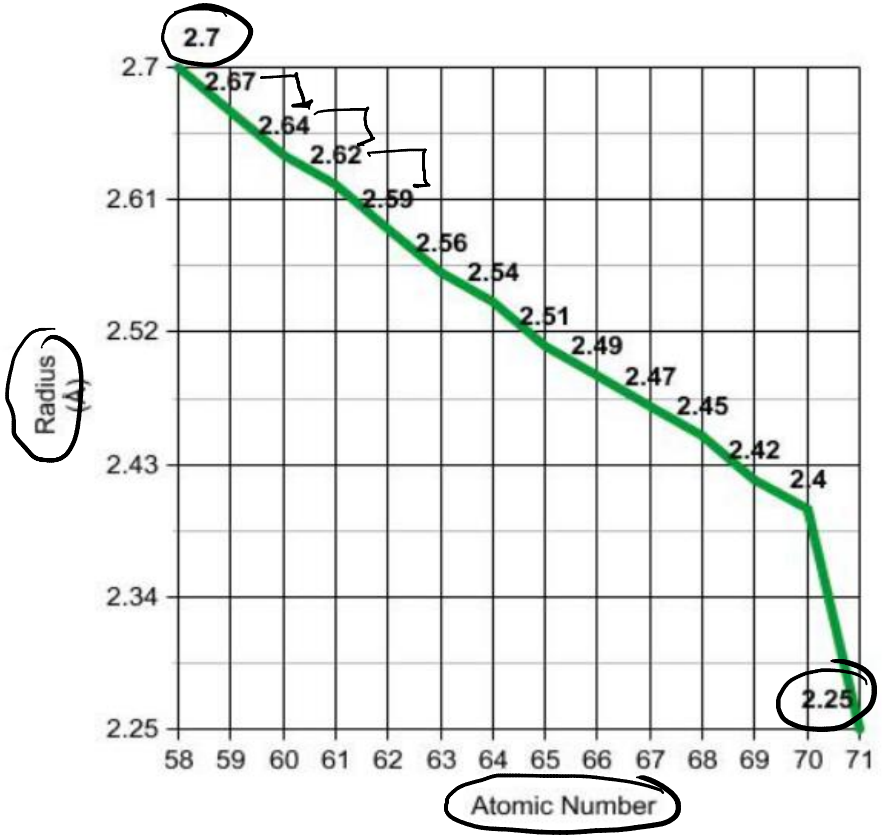
5d La-Lu → Hf → Ta W Re

Same Same Same

due to La-Contrⁿ



2.7 $\xrightarrow{\boxed{0.55}}$ 2.25



La $\xrightarrow{\text{due to La-Contr}^n}$ Lu

57 71

Ⓘ Screening effect ↓

Ⓘⓘ Zeff ↑

Ⓘⓘⓘ atomic Number ↑

} atomic radius ↓ La-Contraction

⇒ atomic No ↑ atomic size ↓

La-Contraction

Factor affecting of lanthanide contraction :

(I) Complex formation ability. ↑

La ⟶ Lu

[Large size element form less complex]

[Small size element form more complex]

② Seperation of the lanthanide elements :

due to the Ln contraction ⇒ Ln Separation is very difficult.

Coordination Number :

Common Co-ordinate No of Last element is greater than >6

Less common: 4, 6

More common: 7 to 12

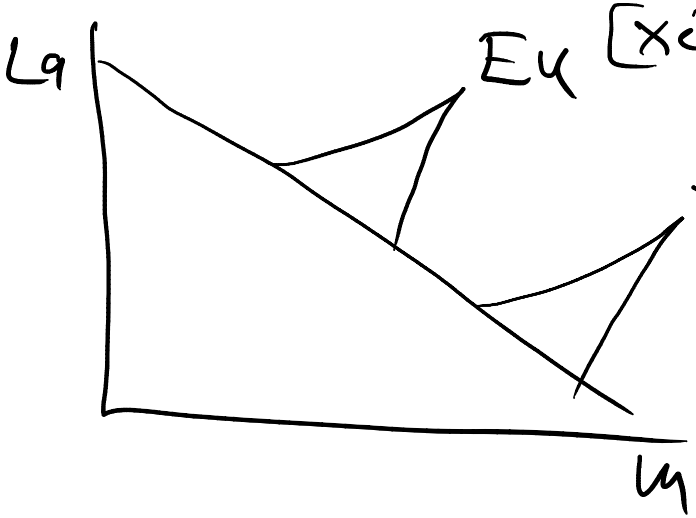
Coordination Number	Complex	Shape
4	$[Lu(2,6\text{-dimethylphenyl})_4]^-$	Tetrahedral
6	$[Ce^{IV}Cl_6]^{2-}$	Octahedral
6	$[Er(NCS)_6]$	Octahedral
7	$[Y(acctylacetone)_3H_2O]$	Mono-capped trigonal prism
8	$[La(acctylacetone)_3(H_2O)_2]$	Square Antiprism
8	$[Eu(acctylacetone)_3(phenanthroline)]$	Square Antiprism
8	$[\overset{8}{Ho}(\overset{2}{tropolonate})_4]^-$	Dodecahedral
9	$[Nd(H_2O)_9]^{3+}$	Tri-capped trigonal prism
10	$\boxed{n=0}$ $4f^0$ $[Ce^{IV}(NO_3)_4(Ph_3PO)_2]$ Diamagnetic $8 + 2 = \boxed{10}$	Complex(each NO_3^- is bidentate)
12	$\boxed{n=0}$ $4f^0$ $[Ce^{IV}(NO_3)_6]^{2-}$ Diamagnet $2\times6 = \boxed{12}$	Icosahedral (each NO_3^- is bidentate)

$n=0$

1. The metallic radii are abnormally high for which of the following pairs?

~~1.~~ Eu, Yb 2. Sm, Tm
3. Gd, Lu 4. Nd, Ho

Ln^0



Eu $[Xe]_{54}\,\underline{\underline{4f^7}}\,6s^2$

Yb $\underline{\underline{4f^{14}}}\,6s^2$

2. The common oxidation state of the elements of lanthanide series is

(1) + 1
~~(2)~~ + 3
(3) + 4
(4) +6

$$\overset{+3}{\text{La}} \longrightarrow \overset{+3}{\text{Lu}}$$

3. The least basic among the following is:

Less basic

Max basic

(1) $Al(OH)_3$ (2) $La(OH)_3$

(3) $Ce(OH)_3$ (4) $Lu(OH)_3$

S-block > Ln > p-block

Na

K

La^{+3}

Ce^{+3}

Lu^{+3}

$\overset{+3}{Al}(OH)_3$

3. For $[Ce(NO_3)_4(OPPh_3)_2]$, from the following

~~A~~. Its aqueous solution is yellow-orange in colour

~~B~~. Coordination number of Ce is ten

~~C~~. It shows metal to ligand charge transfer

~~D~~. It is Diamagnetic in nature the correct answer is:

1. A and B
2. A and C
3. A, B and D
4. B, C and D

(LMCT)

$$\left[\overset{+4}{Ce}(NO_3)_4 (POPh_3)_2 \right]$$

$$8 + 2 = \boxed{10}$$

$$\boxed{C.N = 10}$$

$$\overset{+4}{Ce} = 4f^0$$

[Diamagnetic]

$$\boxed{n = 0}$$

4. Consider the following statements for:

$(NH_4)_2[Ce(NO_3)_6]$ (Z)

~~(a)~~ Coordination number of Ce is 12

~~(b)~~ Z is paramagnetic

~~(c)~~ Z is an oxidising agent

(d) Reaction of Ph_3PO with Z gives a complex having coordination number 10 for Ce.

The correct statements are:

~~1.~~ (a), (b) and (c)

~~2.~~ (b), (a) and (d)

3. (b), (c) and (d)

~~4.~~ (a), (c) and (d)

$[Ce(NO_3)_6]^{-2} + 2P(OPh_3) \longrightarrow Ce(NO_3)_5(POPh_3)_2$

$\boxed{C.N = 12}$

$\boxed{C.N = 10}$

$Ce^{+4} \xrightarrow[e^-]{\text{gain of}} Ce^{+3}$

(Oxidising agent)

Redn

$6\ NO_3 = 2 \times 6 = \boxed{12}$

$(\overset{\oplus}{NH_4})_2 [Ce(NO_3)_6]^{-2}$

$x - 6 = -2$

$x = -2 + 6$

$\boxed{x = +4}$

$Ce^{+4} = 4f^0$

$n = 0$

(Diamagnetic)

5. A comparison of the valence electron configuration of the elements, Sm and Eu suggests that:

~~(1)~~ Sm is a better one electron reductant than Eu
~~(2)~~ Sm is a better one electron oxidant than Eu
(3) Facile oxidation state is +2 for both the elements
~~(4)~~ Both of these display similar redox behaviour.

$Eu^{+3} \xrightarrow{1e^{\ominus}} Eu^{+2} \Rightarrow$ [Reducing agent
Reductant]

$4f^{6}$

$Sm^{+3} \xrightarrow{1e^{\ominus}} Sm^{+2} \Rightarrow$ [Oxidising agent]

$4f^{7}$

Oxidant

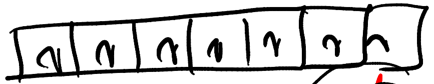
6. The pair of lanthanides with the highest third-ionization energy is:

(a) Eu, Gd (b) Eu, Yb
(c) Dy, Yb (d) Lu, Yb

Eu $[Xe]_{54}\, 4f^{7}\, 6s^{2}\, 5d^{0}$

$\downarrow -2e^{-}$

$4f^{7}$ Eu^{+2}



$\xrightarrow{IE_3}$ max.

Yb $[Xe]_{54}\, 4f^{14}\, 6s^{2}\, 5d^{0}$

$\downarrow$

$4f^{14}$ Yb^{+2} $\xrightarrow{IE_3}$ max IE

7. The metal iodide with metallic lustre and high electrical conductivity is:

1. NaI ✓
2. CdI_2 ✓
[✓ 3. LaI_2]
4. BiI_3 ✓

$ThC_2 \longrightarrow C_2^{-3}$ Ⓟ

Conduct

$CaC_2 \longrightarrow C_2^{-2}$ Ⓓ

Insulator

8. The lanthanide (III) ion having the highest partition coefficient between tri-n-butylphosphate and concentrated HNO_3 is:

(a) La(III) **(b) Eu(III)**
(c) Nd(III) **~~(d)~~ Lu(III)**

La Nd Eu Lu
Larger Smaller

Small Size Ln^{+3} element are more
P.C

9. Statement I. U(VI) is more stable than Nd(VI).
Statement II. The valence electrons in U are in 5f, 6d and 7s orbitals.

(a) Statements I and II are correct and Statement II is correct explanation of I.
[✓ (b) Statements I and II are correct but Statement II is not an explanation for Statement I.]
(c) Statement I is correct and Statement II is incorrect.
(d) Statements I and II both are incorrect.

20. The coordination number and geometry of cerium in $[Ce(NO_3)_6]^{2-}$ are respectively:

(1) 6 and octahedron
(2) 6 and trigonal prism
(3) 8 and cubic
(4) 12 and icosahedron

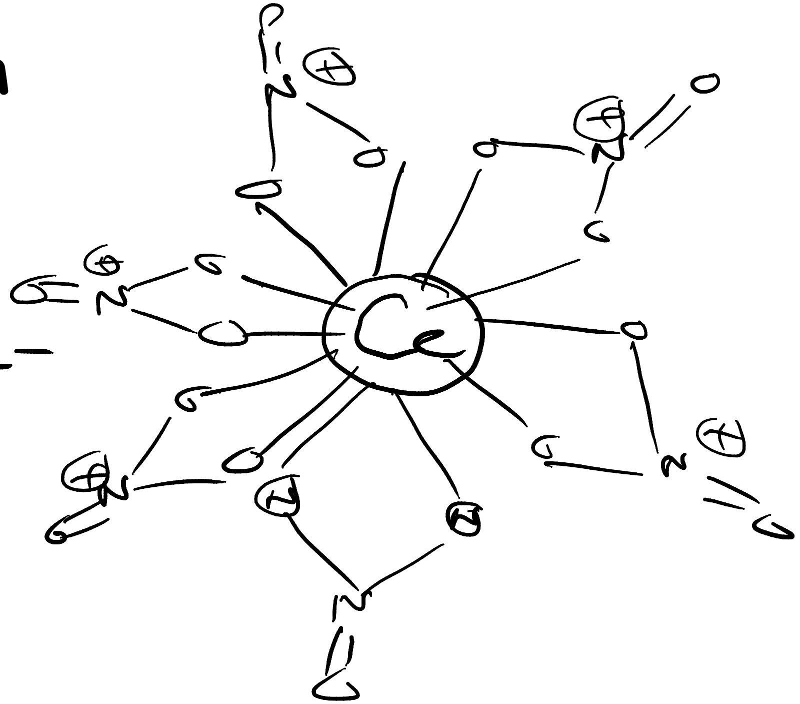
$\left[Ce(NO_3)_6\right]^{2-}$

$\Downarrow$

$2 \times 6 = \boxed{12}$

$\boxed{CN = 12}$

[Icosahedran]



22. The electronic configuration for gadolinium (Gd) is [Xe] $4f^7 5d^1 6s^2$, where as that of $Gd^{\textcircled{2+}}$ is:

(a) [Xe] $4f^5 5d 6s^2$ **(b) [Xe] $4f^6 6s^2$**

(c) [Xe] $4f^6 5d^1 6s^1$ **~~(d)~~ [Xe] $4f^7 5d^1$**

$[Xe]_{54}\ 4f^{7}\ \underline{\underline{5d^{1}}}\ \underline{\underline{6s^{\textcircled{2}}}} \Rightarrow Gd$

$(n+l)$

$\underline{\underline{6s}} = (6+0) = \textcircled{6}$

$5d = 5+2 = 7$

$\downarrow$

$Gd^{+2}\ 4f^{7}\ 5d^{1}$

23. Statement I: The sizes of Zr and Hf are similar
Statement II: Size of Hf is affected by lanthanide contraction.

(1) Statement I and II are correct and II is correct explanation of I.

(2) Statement I and II are correct but II is not a correct explanation of I.

(3) Statement I is correct and II is incorrect

(4) Statements I and II both are incorrect.

2. The lanthanide complex (acac = acetylacetonate; phen = 1, 10-phennathroline) that do not have square antiprismatic structure is

[C.N= 8]

~~(1)~~ $[Ce(NO_3)_6]^{2-}$ $\boxed{C.N= 12}$
(b) $[La(acac)_3 (H_2O)_2]$ (C.N= 8)
(c) $[Ce(acac)_4]$ (C.N= 8)
(d) $[Eu(acac)_3Phen]$ C.N= 8

C.N= 8

THANK YOU