

TRANSITION & INNER TRANSITION ELEMENTS



Lecture 7.

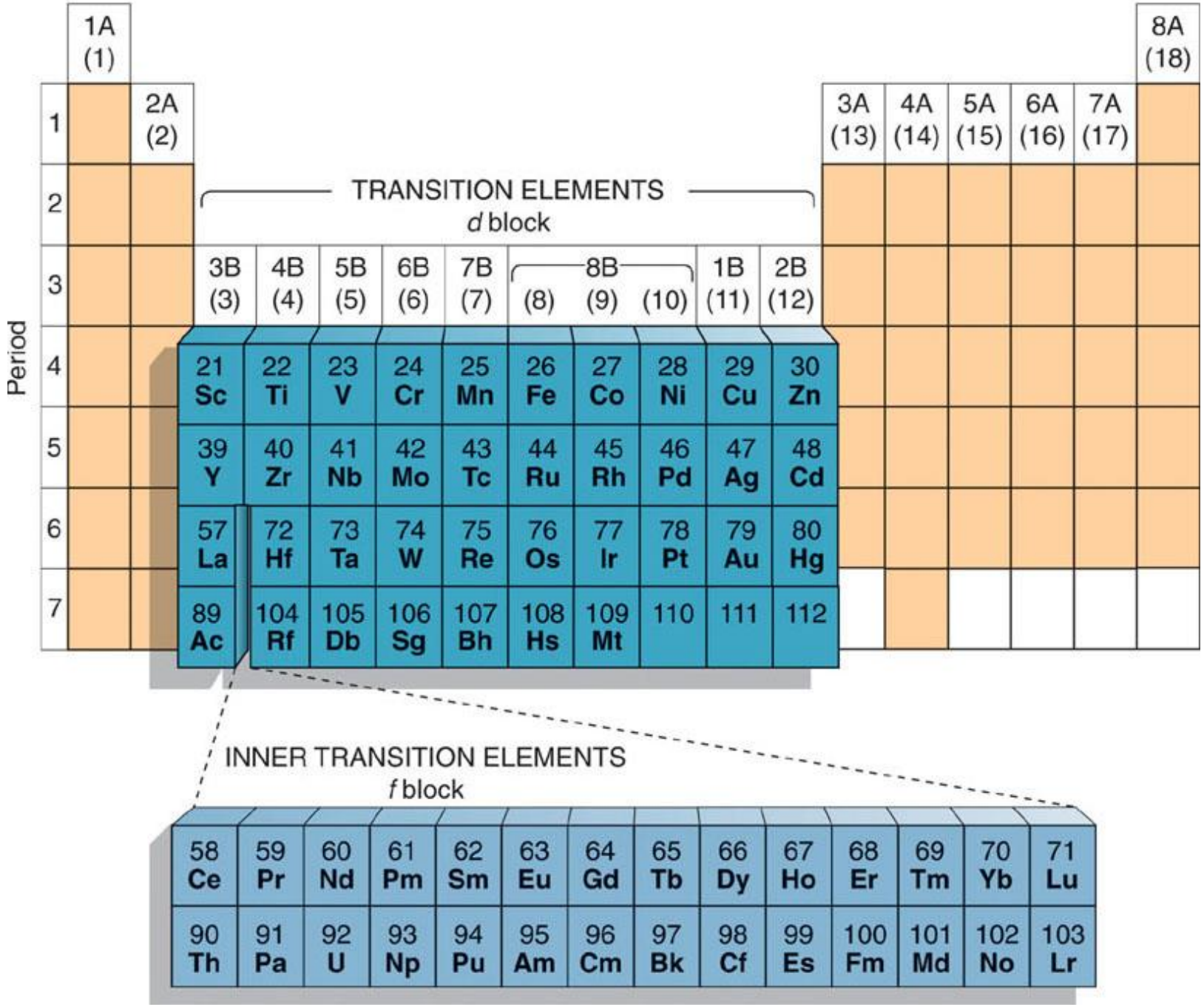


Q. 1 – Which oxide is the most & least basic in the entire Lanthanide series?

Answer:

1. $La(OH)_3$ & $Lu(OH)_3$



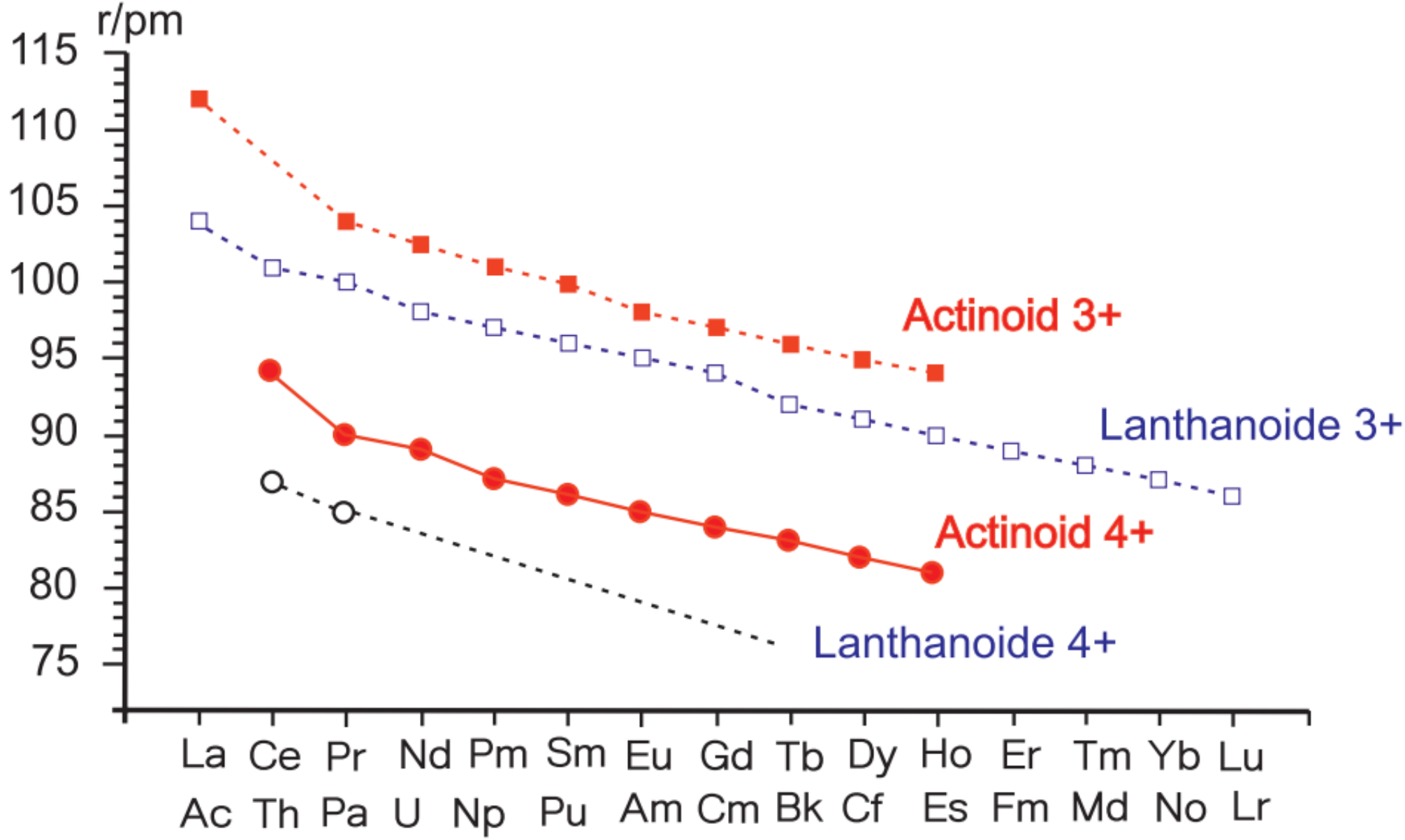

1A (1)
8A (18)
2A (2)
3A (13)
4A (14)
5A (15)
6A (16)
7A (17)
TRANSITION ELEMENTS
d block
3B (3)
4B (4)
5B (5)
6B (6)
7B (7)
8B
(8) (9) (10)
1B (11)
2B (12)
Period
1 2 3 4 5 6 7
21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn
39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd
57 La 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 110 111 112
INNER TRANSITION ELEMENTS
f block
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

PROPERTIES OF ACTINOIDS:

1. Similar to Lanthanoids, they are silvery-white in colour.
2. They have high density.
3. They are less reactive than Lanthanoids.
4. Most of the Actinoids are not found in the nature i.e. they are man-made.
5. They are highly reactive radioactive elements.
6. They have high boiling (≈ 3000 °C) & melting points (≈ 1000 °C).
7. Atomic & ionic radii decreases from Actinium (Ac) to Lawrencium (Lr). {This effect is called as Actinoid Contraction}
8. They show a common oxidation state of +3.
9. They can exhibit a wide range of oxidation states right from +2 to +8.
10. Basic nature of the oxides reduces from $Ac(OH)_3$ to $Lr(OH)_3$.
11. Action of boiling water gives mixture of oxides and hydroxides.

ATOMIC AND IONIC RADII: THE ACTINOID CONTRACTION

- As we move along the actinide series, there is a decrease in the atomic & ionic radii.
- With increasing atomic number, each succeeding element contains one more electron and one proton in the nucleus.
- The incoming electron is added to the same inner 5f subshell.
- The 5f electrons are ineffective in screening, due to their diffused shape, the outer electrons from the nucleus causing imperfect shielding.
- As a result, there is a gradual increase in the nucleus attraction for the outer electrons.
- Consequently gradual decrease in size occur.
- This is called actinide contraction.


r/pm
115
110
105
100
95
90
85
80
75
Actinoid 3+
Lanthanoide 3+
Actinoid 4+
Lanthanoide 4+
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

ACTINOIDS

Element	Symbol	Atomic number	Electronic configuration		*Atomic radii, pm	*Ionic radii ($Ac^{3\oplus}$), pm
			ground state	+3 oxidation state		
Actinium	Ac	89	$[Rn]5f^{0}6d^{1}7s^{2}$	$5f^{0}$	203	126
Thorium	Th	90	$[Rn]5f^{0}6d^{2}7s^{2}$	$5f^{1}$	180	-
Protactinium	Pa	91	$[Rn]5f^{2}6d^{1}7s^{2}$	$5f^{2}$	162	118
Uranium	U	92	$[Rn]5f^{3}6d^{1}7s^{2}$	$5f^{3}$	153	118
Neptunium	Np	93	$[Rn]5f^{4}6d^{1}7s^{2}$	$5f^{4}$	150	116
Plutonium	Pu	94	$[Rn]5f^{6}6d^{0}7s^{2}$	$5f^{5}$	162	115
Americium	Am	95	$[Rn]5f^{7}6d^{0}7s^{2}$	$5f^{6}$	173	114
Curium	Cm	96	$[Rn]5f^{7}6d^{1}7s^{2}$	$5f^{7}$	174	112
Berkelium	Bk	97	$[Rn]5f^{9}6d^{0}7s^{2}$	$5f^{8}$	170	110
Californium	Cf	98	$[Rn]5f^{10}6d^{0}7s^{2}$	$5f^{9}$	186	109
Einsteinium	Es	99	$[Rn]5f^{11}6d^{0}7s^{2}$	$5f^{10}$	186	98
Fermium	Fm	100	$[Rn]5f^{12}6d^{0}7s^{2}$	$5f^{11}$	198	91
Mendelevium	Md	101	$[Rn]5f^{13}6d^{0}7s^{2}$	$5f^{12}$	194	90
Nobelium	No	102	$[Rn]5f^{14}6d^{0}7s^{2}$	$5f^{13}$	197	95
Lawrencium	Lr	103	$[Rn]5f^{14}6d^{1}7s^{2}$	$5f^{14}$	171	88

- $_{89}$Ac = [Rn] $\mathbf{7s^2\ 5f^0\ 6d^1}$
- $_{90}$Th = [Rn] $\mathbf{7s^2\ 5f^0\ 6d^2}$
- $_{91}$Pa = [Rn] $\mathbf{7s^2\ 5f^2\ 6d^1}$
- $_{92}$U = [Rn] $\mathbf{7s^2\ 5f^3\ 6d^1}$
- $_{93}$Np = [Rn] $\mathbf{7s^2\ 5f^4\ 6d^1}$
- $_{94}$Pu = [Rn] $\mathbf{7s^2\ 5f^5\ 6d^1}$
- $_{95}$Am = [Rn] $\mathbf{7s^2\ 5f^7\ 6d^0}$
- $_{96}$Cm = [Rn] $\mathbf{7s^2\ 5f^7\ 6d^1}$

- $_{97}$Bk = [Rn] $\mathbf{7s^2\ 5f^9\ 6d^0}$
- $_{98}$Cf = [Rn] $\mathbf{7s^2\ 5f^{10}\ 6d^0}$
- $_{99}$Es = [Rn] $\mathbf{7s^2\ 5f^{11}\ 6d^0}$
- $_{100}$Fm = [Rn] $\mathbf{7s^2\ 5f^{12}\ 6d^0}$
- $_{101}$Md = [Rn] $\mathbf{7s^2\ 5f^{13}\ 6d^0}$
- $_{102}$No = [Rn] $\mathbf{7s^2\ 5f^{14}\ 6d^0}$
- $_{103}$Lr = [Rn] $\mathbf{7s^2\ 5f^{14}\ 6d^1}$

They have general valence shell electronic configuration of $\mathbf{ns^2\ (n\text{-}1)d^{0\text{-}2}\ (n\text{-}2)f^{0,2\text{-}14}}$.

MNEMONIC TO MEMORIZE ACTINOIDS.

- Actor Thor Protects Uranus Neptune & Pluto while America Cures Berkley in California from Einstein's Fermi's & Mendeleev's Noble Laws.

- Elements covered = Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr.

Pre-Transition Metals	Lanthanoids	Transition Metals
Essentially monovalent - show group (n+) oxidation state	Essentially in (+3) oxidation state (+2/+4 for certain configurations)	Show variable oxidation states
Periodic trends dominated by effective nuclear charge at noble gas configuration	Lanthanoid contraction of $Ln^{3\oplus}$	Size changes of $M^{n\oplus}$, less marked
Similar properties for a given group	Similar properties	Substantial changes in properties
Always 'hard' (O, X, N donors, preferably negatively charged)	Always 'hard' (O, X, N donors, preferably negatively charged)	heavier metals (increasingly from Fe-Cu) may show a 'soft' character
No ligand field effects	Insignificant ligand field effects	Substantial ligand field effects
Poor coordination properties(C.N. determined by size)	High coordination numbers (C.N. determined by size)	Coordination number 6 is typical maximum (many exceptions)
Flexibility in geometry	Flexibility in geometry	Fixed geometries (ligand field effects)
No magnetism	Show magnetism	Show magnetism

Similarities	Differences
Both the series show a +3 oxidation state	Lanthanoids show a maximum oxidation state of +4 while actinoids show oxidation states of +3, +4, +5, +6 and +7
In both the series, the f-orbitals are filled gradually	Lanthanoids do not form complexes easily. Actinoids have a greater tendency to form complexes with ligands such as thio-ethers
Ionic radius of the elements in both series decreases with an increase in atomic number	All lanthanoids are non-radioactive except promethium but actinides are radioactive in nature
The electronegativity of all the elements in both the series is low and are said to be highly reactive	Lanthanoids do not form oxocations, but actinides form oxocations such as UO^{+}, PuO^{+}, NpO_2^{+}
The nitrates, perchlorates and sulphates of all the elements are soluble while the hydroxides, fluorides and carbonates are insoluble	Most of the lanthanoids are colourless in nature whereas the actinoids are coloured ions

APPLICATION:

1. Because of their long half-lives, Thorium & Uranium are used in everyday life.
2. THO_2, along with 1% CeO_2 ,is used as a major source of indoor lighting.
3. Uranium is used as a nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry, ceramic industry and in medicines.
4. Plutonium it is used as a fuel for atomic reactors as well as for making atomic bombs.

Any Question



“It is not the answer that enlightens, but the question.”

- Eugene Ionesco