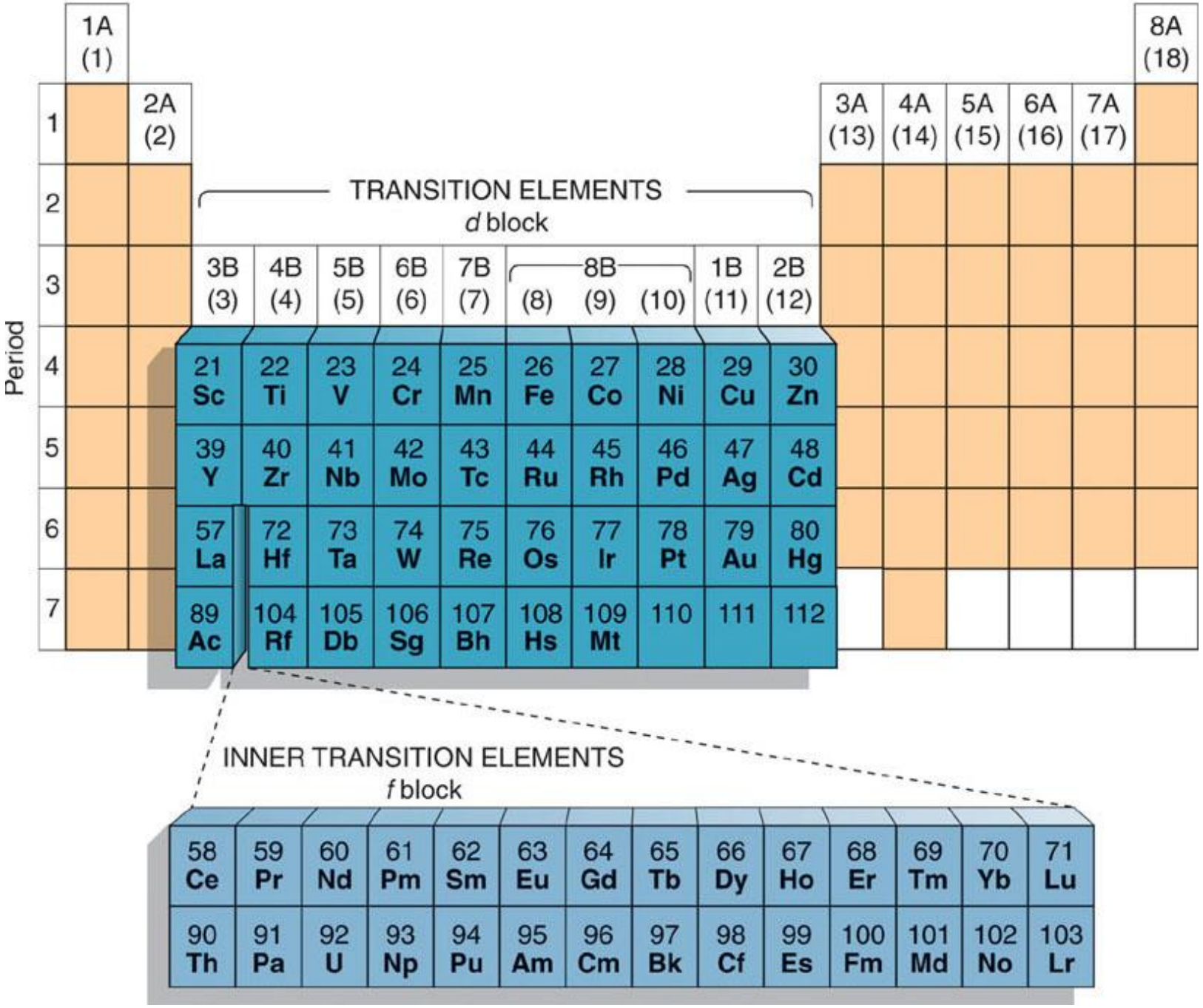
TRANSITION & INNER TRANSITION ELEMENTS

Lecture 6.

Q. 1 – What is the general oxidation state shown by Lanthanoids?

Answer:

1. +3


1A (1)
2A (2)
3A (13)
4A (14)
5A (15)
6A (16)
7A (17)
8A (18)
Period
1
2
3
4
5
6
7
TRANSITION ELEMENTS
d block
3B (3)
4B (4)
5B (5)
6B (6)
7B (7)
8B
(8) (9) (10)
1B (11)
2B (12)
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

Element	Symbol	Atomic number	Electronic configuration				Atomic radii, pm	Ionic radii (Ln^{+3}, 6-coordinate), pm
			Expected (ground state)	Observed (ground state)	(+2 oxidation state)	(+3 oxidation state)		
Lanthanum	La	57	$[Xe]4f^{0}5d^{1}6s^{2}$	$[Xe]4f^{0}5d^{1}6s^{2}$	$4f^{0}$	$4f^{0}$	187	103
Cerium	Ce	58	$[Xe]4f^{2}6s^{2}$	$[Xe]4f^{1}5d^{1}6s^{2}$		$4f^{1}$	183	102
Praseodymium	Pr	59	$[Xe]4f^{3}6s^{2}$	$[Xe]4f^{3}6s^{2}$	$4f^{2}$	$4f^{2}$	182	99
Neodymium	Nd	60	$[Xe]4f^{4}6s^{2}$	$[Xe]4f^{4}6s^{2}$			181	98.3
Promethium	Pm	61	$[Xe]4f^{5}6s^{2}$	$[Xe]4f^{5}6s^{2}$	$4f^{4}$		181	97
Samarium	Sm	61	$[Xe]4f^{6}6s^{2}$	$[Xe]4f^{6}6s^{2}$	$4f^{5}$	$4f^{5}$	180	95.8
Europium	Eu	63	$[Xe]4f^{7}6s^{2}$	$[Xe]4f^{7}6s^{2}$		$4f^{6}$	199	94.7
Gadolinium	Gd	64	$[Xe]4f^{8}6s^{2}$	$[Xe]4f^{7}5d^{1}6s^{2}$	$4f^{7}$		178	93.8
Terbium	Tb	65	$[Xe]4f^{9}6s^{2}$	$[Xe]4f^{9}6s^{2}$		$4f^{8}$	177	92.3
Dysprosium	Dy	66	$[Xe]4f^{10}6s^{2}$	$[Xe]4f^{10}6s^{2}$		$4f^{9}$	176	91.2
Holmium	Ho	67	$[Xe]4f^{11}6s^{2}$	$[Xe]4f^{11}6s^{2}$	$4f^{10}$	$4f^{10}$	175	90.1
Erbium	Er	68	$[Xe]4f^{12}6s^{2}$	$[Xe]4f^{12}6s^{2}$			174	89
Thulium	Tm	69	$[Xe]4f^{13}6s^{2}$	$[Xe]4f^{13}6s^{2}$	$4f^{12}$	$4f^{12}$	173	88
Ytterbium	Yb	70	$[Xe]4f^{14}6s^{2}$	$[Xe]4f^{14}6s^{2}$	$4f^{13}$			86.8
Lutetium	Lu	71	$[Xe]4f^{145}d^{1}6s^{2}$	$[Xe]4f^{145}d^{1}6s^{2}$		$4f^{14}$		86.1

Why F-block Elements Placed Outside Separately?

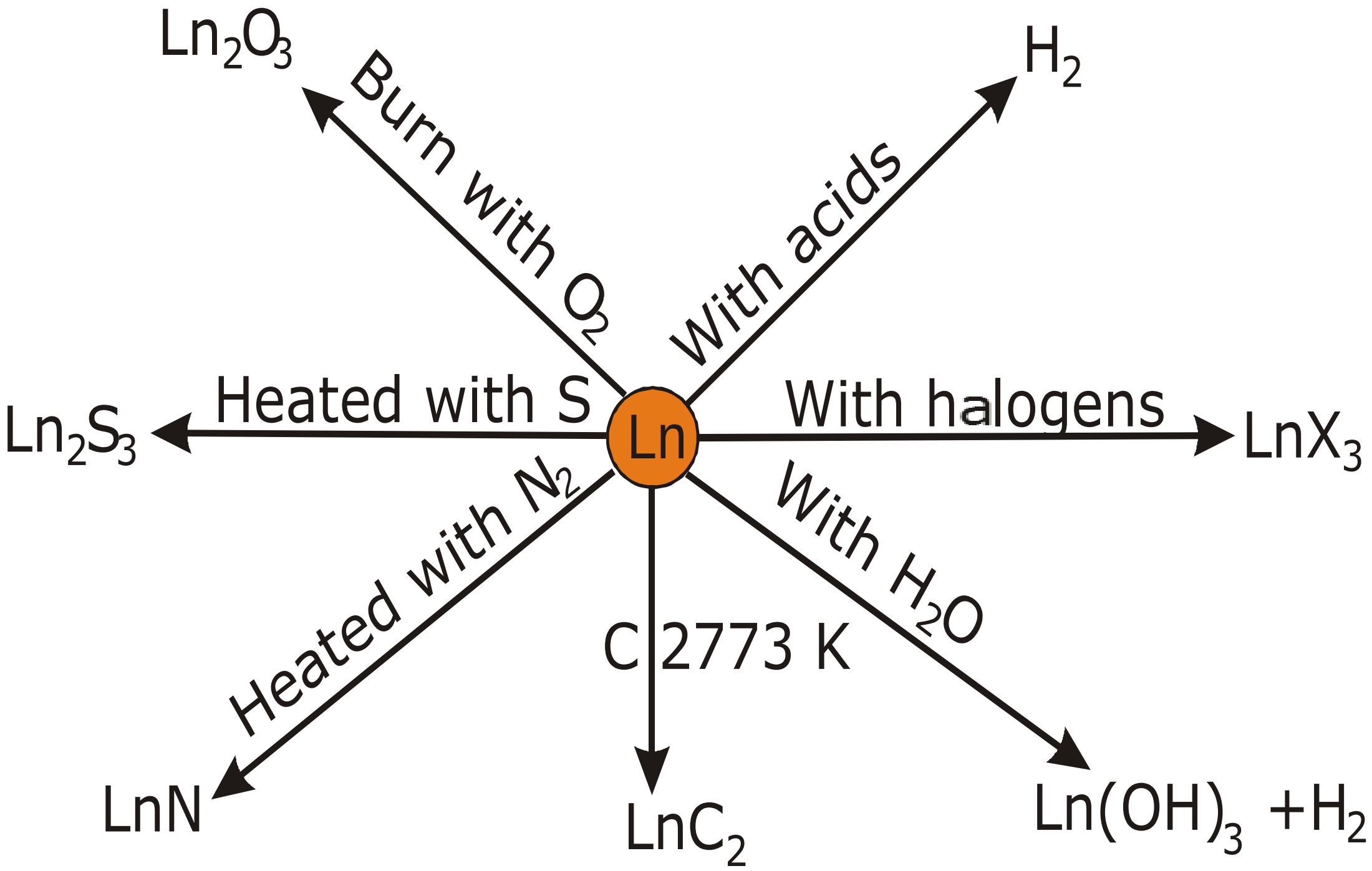
- The reason for this is the remarkable similarities among the chemical properties of the Lanthanoids and also among the various members of Actinoids.
- The similarities in properties, in turn, is due to the similar electronic configuration of the outermost shell.
- These elements differ only in the number of f-electrons which do not take part in chemical bonding.

PROPERTIES OF LANTHANOIDS:

1. They are soft metals with silvery-white colour & moderate densities.
2. They are good conductors of heat and electricity.
3. Except Promethium all the remaining elements are non-radioactive.
4. Atomic & ionic radii decreases from Lanthanum (La) to Lutetium (Lu). {This effect is called as Lanthanoid Contraction}
5. Binding to water is common.
6. Co-ordination number is usually higher than 6 (8/9/..12) eg: $[La(H_2O)_9]^{3+}$
7. They are strongly paramagnetic.
8. Magnetic & optical properties are independent of environment.
9. They show a common oxidation state of +3.
10. Basic nature of the oxides reduces from $La(OH)_3$ to $Lu(OH)_3$.

PROPERTIES OF LANTHANOIDS:

1. They have high boiling (≈ 3000 °C) & melting points (≈ 1000 °C).
2. They combine with water to give metal hydroxide and Hydrogen gas.
3. LnC_2 is formed when they are heated with carbon around 2800 K.
4. They react with Nitrogen & Halogens to form nitrides & halides of the formulae LnN & LnX_3.
5. They form oxides and hydroxides, M_2O_3 and $M(OH)_3$, which are basic like alkaline earth metal oxides and hydroxides.


Ln
Burn with O_2
Ln_2O_3
With acids
H_2
Heated with S
Ln_2S_3
With halogens
LnX_3
Heated with N_2
LnN
C 2773 K
LnC_2
With H_2O
$Ln(OH)_3 + H_2$

OXIDATION STATES:

Predominantly +3 oxidation state.

This irregularity arises mainly from the extra stability of empty, half filled or filled f subshell.

Occasionally +2 and +4 are also obtained.

COLOUR:

Oxidation state	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
+2						Sm^{2+}	Eu^{2+}						Tm^{2+}	Yb^{2+}	
+3	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
+4		Ce^{4+}	Pr^{4+}	Nd^{4+}					Tb^{4+}	Dy^{4+}					

- The colour of ions having ‘nf’ electrons is same as those having ‘(14-n)f’ electrons.

  Where, n = 1-13

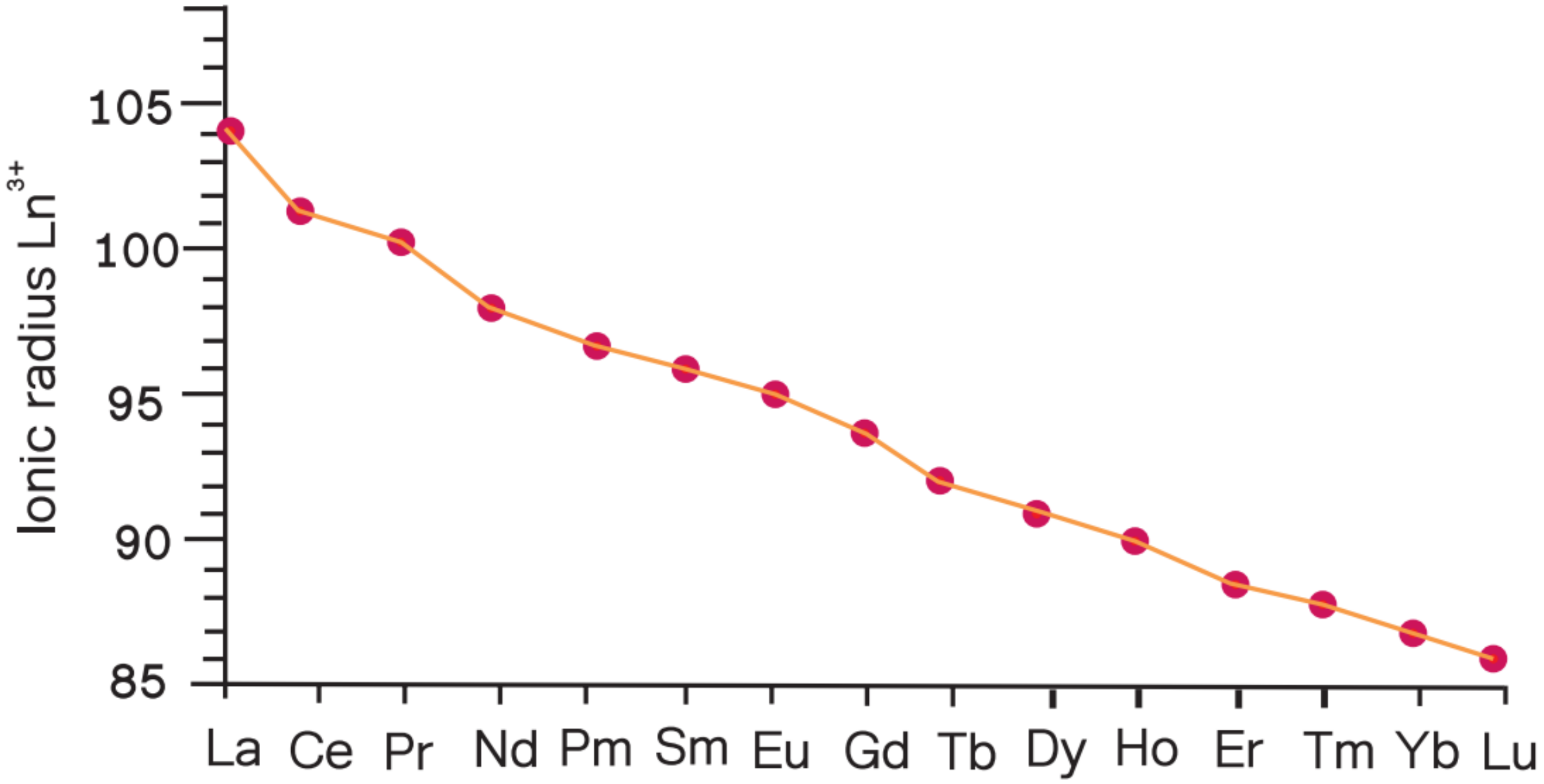
- Colour of Lanthanoid ions is due to f – f transitions which corresponds to energy in the visible region.
- The trivalent lanthanide ions are coloured both in the solid state and in aqueous solution.
- The colours are unchanged even on alteration of the anions/ligands indicating that they are characteristic of the cations.

MAGNETIC MOMENT:

Ln	Ln^{3+} oxidation state	No. of unpaired electrons	Observed magnetic moment, $\mu_{eff\ B.M}$
La	$4f^0$	0	0
Ce	$4f^1$	1	2.3-2.5
Pr	$4f^2$	2	3.4-3.6
Nd	$4f^3$	3	3.5-3.6
Pm	$4f^4$	4	--
Sm	$4f^5$	5	1.4-1.7
Eu	$4f^6$	6	3.3-3.5
Gd	$4f^7$	7	7.9-8.0
Tb	$4f^8$	6	9.5-9.8
Dy	$4f^9$	5	10.4-10.6
Ho	$4f^{10}$	4	10.4-10.7
Er	$4f^{11}$	3	9.4-9.6
Tm	$4f^{12}$	2	7.1-7.6
Yb	$4f^{13}$	1	4.3-4.9
Lu	$4f^{14}$	0	0

ATOMIC AND IONIC RADII: THE LANTHANIDE CONTRACTION

- As we move along the lanthanide 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 4f subshell.
- The 4f 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 lanthanide contraction.

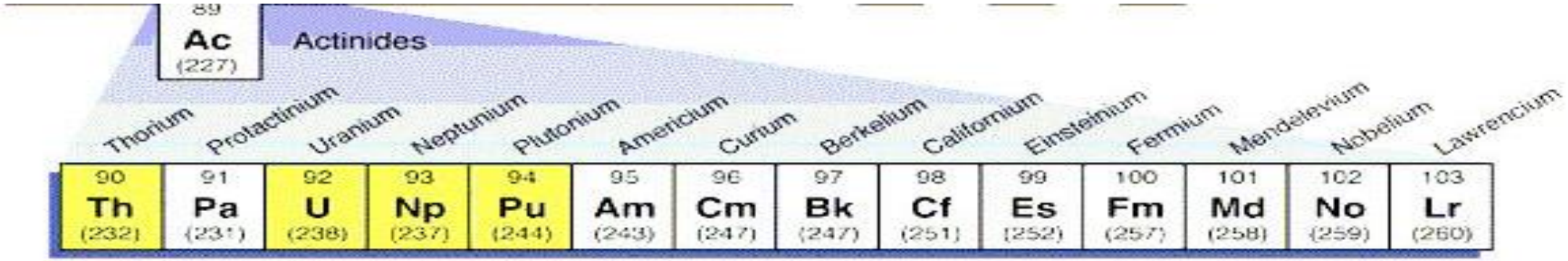

Ionic radius Ln^{3+}
105
100
95
90
85
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

APPLICATION:

1. Present in the television & computer monitor to give colour (RGB).
2. Mixed oxide of Yttrium & Europium $(Eu,Y)_2O_3$ releases intense red colour when bombarded with high energy electrons.
3. Nd:YAG laser (Neodymium doped Yttrium Aluminium Garnet)
4. Erbium doped fibre amplifiers are used in optical fibre communication systems.
5. Used in hybrid cars, superconductors & permanent magnets.
6. A well known alloy is misch metal which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of misch metal is used in Mg based alloy to produce bullets, shell and lighter flint.
7. Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking.

Actinoids (5f-series):

The actinoids include the fourteen elements from Th to Lr. The actinoids are radioactive elements and the earlier members have relatively long half lives, the latter ones have half life values ranging from a day to 3 minutes for lawrencium (Z=103).



Next Lecture:

1. Trends in the properties of F-block elements.

Any Question

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

- Eugene Ionesco