

CHEMISTRY OF F-BLOCK ELEMENTS

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Reference Books

- ❖ Inorganic Chemistry For B.Sc. Of all Indian Universities By R.L.Madan and G.D.Tuli.
- ❖ Inorganic Chemistry by Catherine E.Housecraft and Alan G.Sharpe.
- ❖ Inorganic Chemistry Principles of Structure and Reactivity By James E.Huheey, Ellen A.Keiter, Richard L.Keiter.
- ❖ Concise of Inorganic Chemistry By J.D.Lee

Introduction:

Periodic Table of the Elements 2005

1 H 1.01																	18 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 25.31											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 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	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 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

POSITION IN PERIODIC TABLE

Their position are as follow.

PERIODIC TABLE

If we put **lanthanides and actinides** in to the **Periodic Table** like transition metals, the **table** will be way too wide. The two rows of elements present at the bottom of the **periodic table** are called the 4f series or lanthanoids and 5f or actanoids. They are also called inner transition elements.

Representative Elements (s-block)

Transition Elements (d-block)

Representative Elements (p-block)

Noble gases

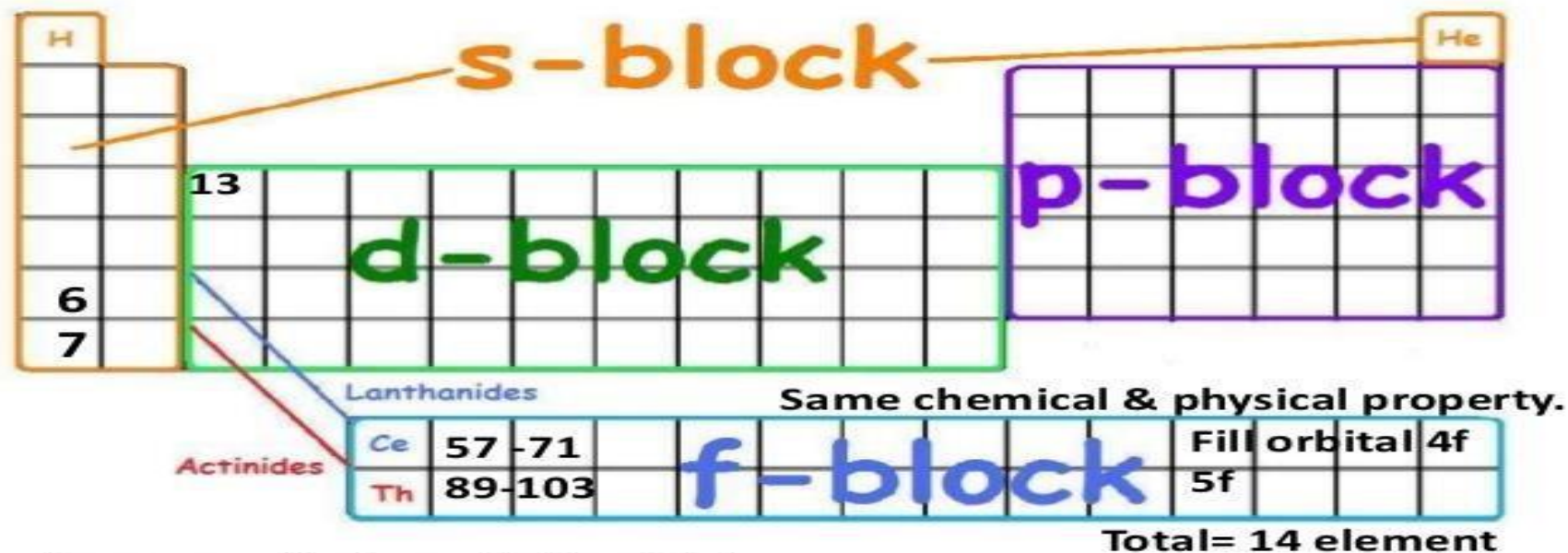
PERIODS

1	H	2											13	14	15	16	17	18
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt									

Inner Transition Elements (f-block)

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

Position of lanthanoids



Same no. of valency $5d^1$ and $6s^2$.

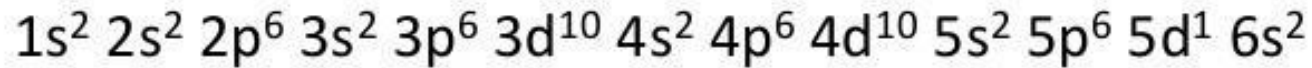
Hydrogen 1 H 1.008																	Helium 2 He 4.003	
Lithium 3 Li 6.941	Beryllium 4 Be 9.012																	
Sodium 11 Na 22.990	Magnesium 12 Mg 24.305																	
Potassium 19 K 39.098	Calcium 20 Ca 40.078	Scandium 21 Sc 44.956															Titanium 22 Ti 47.88	Vanadium 23 V 50.942
Rubidium 37 Rb 85.468	Sr 38 Sr 87.62	Y 39 Y 88.906															Zirconium 40 Zr 91.224	Niobium 41 Nb 92.906
Cesium 55 Cs 132.905	Ba 56 Ba 137.327	Lanthanum 57 La 138.905	Ce 58 Ce 140.115	Pr 59 Pr 140.908	Nd 60 Nd 144.24	Pm 61 Pm 144.913	Sm 62 Sm 150.36	Eu 63 Eu 151.964	Gd 64 Gd 157.25	Tb 65 Tb 158.925	Dy 66 Dy 162.5	Ho 67 Ho 164.930	Er 68 Er 167.26	Tm 69 Tm 168.934	Yb 70 Yb 173.054	Lu 71 Lu 174.967	Hf 72 Hf 178.49	Ta 73 Ta 180.948
Francium 87 Fr 223.028	Ra 88 Ra 226.025	Actinium 89 Ac 227.028	Th 90 Th 232.038	Pa 91 Pa 231.036	U 92 U 238.029	Np 93 Np 237.048	Pu 94 Pu 244.064	Am 95 Am 243.061	Cm 96 Cm 247.070	Bk 97 Bk 247.070	Cf 98 Cf 251.080	Es 99 Es 252.083	Fm 100 Fm 257.10	Md 101 Md 258.10	No 102 No 259.10	Lr 103 Lr 260.10	Rf 104 Rf 261.10	Db 105 Db 262.10

- The elements in which the additional electrons enter $(n-2)f$ orbitals are called **inner transition elements**. The valence shell electronic configuration of these elements can be represented as $(n - 2)f^{0-14}(n - 1)d^{0-1}ns^2$.
- 4f inner transition metals are known as lanthanides because they come immediately after lanthanum and 5f inner transition metals are known as actinoids because they come immediately after actinium.

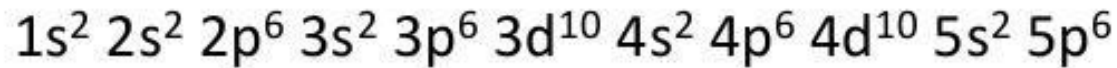
Electronic configuration of lanthanoids

- E.C Based on aufbau principle .

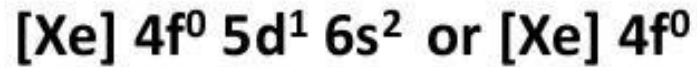
La (57)



[Xe] – 54



The electronic configuration of Ln is



Similarly **Ce- $4f^1$, Pr- $4f^2$,..... Lu- $4f^{14}$.(expected)**

but **observed** E.C is not true for all element.

The elements in which the additional electrons enters (n-2)f orbitals are called **inner transition elements**. The valence shell electronic configuration of these elements can be represented as **$(n - 2)f^{0-14}(n - 1)d^{0-1}ns^2$** .

Electronic Configuration

Element name	Symbol	Z	Ln	Ln ³⁺	Radius Ln ³⁺ / pm
Lanthanum	La	57	[Xe]6s ² 5d ¹	[Xe]4f ⁰	116
Cerium	Ce	58	[Xe]4f ¹ 6s ² 5d ¹	[Xe]4f ¹	114
Praesodymium	Pr	59	[Xe]4f ³ 6s ²	[Xe]4f ²	113
Neodymium	Nd	60	[Xe]4f ⁴ 6s ²	[Xe]4f ³	111
Promethium	Pm	61	[Xe]4f ⁵ 6s ²	[Xe]4f ⁴	109
Samarium	Sm	62	[Xe]4f ⁶ 6s ²	[Xe]4f ⁵	108
Europium	Eu	63	[Xe]4f ⁷ 6s ²	[Xe]4f ⁶	107
Gadolinium	Gd	64	[Xe]4f ⁷ 6s ² 5d ¹	[Xe]4f ⁷	105
Terbium	Tb	65	[Xe] 4f ⁹ 6s ²	[Xe]4f ⁸	104
Dysprosium	Dy	66	[Xe] 4f ¹⁰ 6s ²	[Xe]4f ⁹	103
Holmium	Ho	67	[Xe] 4f ¹¹ 6s ²	[Xe]4f ¹⁰	102
Erbium	Er	68	[Xe] 4f ¹² 6s ²	[Xe]4f ¹¹	100
Thulium	Tm	69	[Xe] 4f ¹³ 6s ²	[Xe]4f ¹²	99
Ytterbium	Yb	70	[Xe] 4f ¹⁴ 6s ²	[Xe]4f ¹³	99
Lutetium	Lu	71	[Xe] 4f ¹⁴ 6s ² 5d ¹	[Xe]4f ¹⁴	98

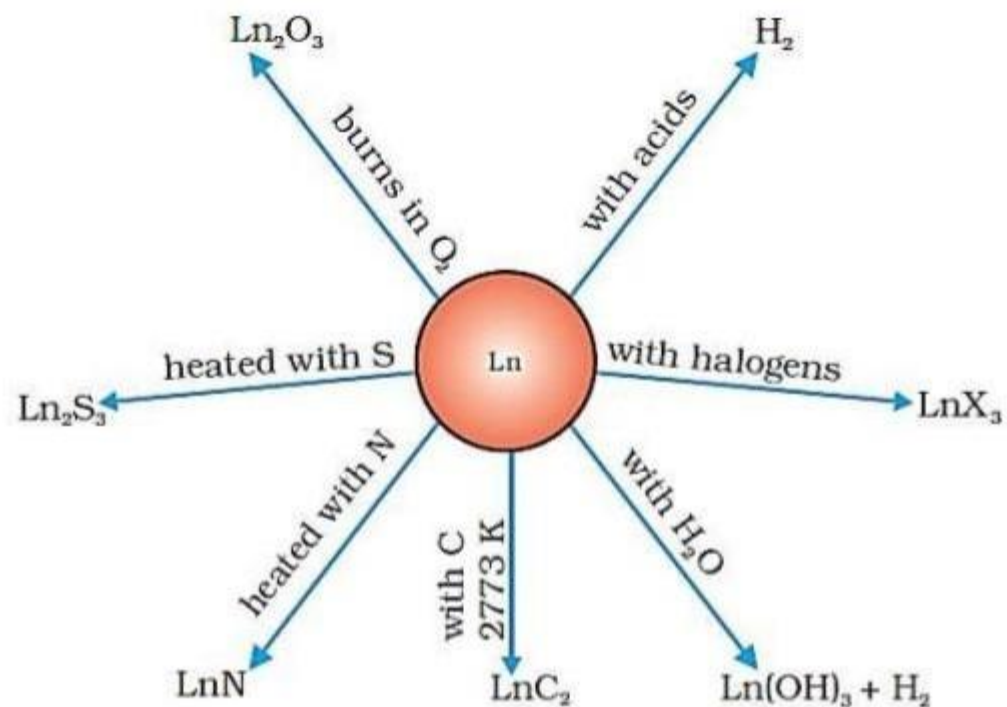
Lanthanides

Lanthanide	Chemistry	Presents	No	Problems	Since	Everyone	Goes	To	Doctor	Heyes'	Excruciatingly	Thorough	Yearly	Lectures
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

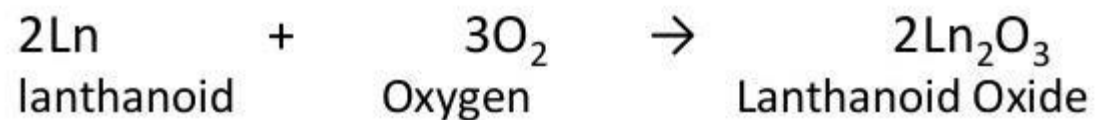
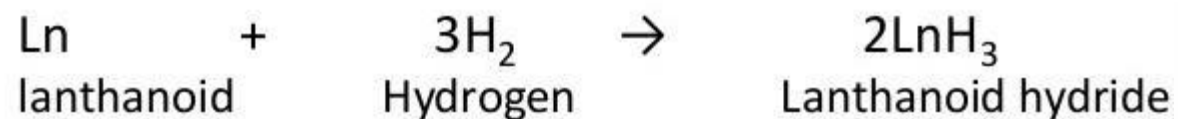
Oxidation state

Symbol	Idealized	Observed	M ³⁺	M ²⁺	M ⁺
La	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe] 4f ⁰ 5d ¹ 6s ²	[Xe]	-	
Ce	[Xe]4f ¹ 5d ¹ 6s ²	[Xe]4f ² 5d ⁰ 6s ²	4f ¹	4f ²	[Xe]
Pr	[Xe]4f ² 5d ¹ 6s ²	[Xe]4f ³ 5d ⁰ 6s ²	4f ²	-	4f ¹
Nd	[Xe]4f ³ 5d ¹ 6s ²	[Xe]4f ⁴ 6s ²	4f ³	4f ⁴	4f ²
Pm	[Xe]4f ⁴ 5d ¹ 6s ²	[Xe]4f ⁵ 6s ²	4f ⁴	-	-
Sm	[Xe]4f ⁵ 5d ¹ 6s ²	[Xe]4f ⁶ 6s ²	4f ⁵	4f ⁶	-
Eu	[Xe]4f ⁶ 5d ¹ 6s ²	[Xe]4f ⁷ 6s ²	4f ⁶	4f ⁷	-
Gd	[Xe]4f ⁷ 5d ¹ 6s ²	[Xe]4f ⁷ 5d ¹ 6s ²	4f ⁷	-	-
Tb	[Xe]4f ⁸ 5d ¹ 6s ²	[Xe]4f ⁹ 6s ²	4f ⁸	-	4f ⁷
Dy	[Xe]4f ⁹ 5d ¹ 6s ²	[Xe]4f ¹⁰ 6s ²	4f ⁹	-	4f ⁸
Ho	[Xe]4f ¹⁰ 5d ¹ 6s ²	[Xe]4f ¹¹ 6s ²	4f ¹⁰	-	-
Er	[Xe]4f ¹¹ 5d ¹ 6s ²	[Xe]4f ¹² 6s ²	4f ¹¹	-	-
Tm	[Xe]4f ¹² 5d ¹ 6s ²	[Xe]4f ¹³ 6s ²	4f ¹²	4f ¹³	-
Yb	[Xe]4f ¹³ 5d ¹ 6s ²	[Xe]4f ¹⁴ 6s ²	4f ¹³	4f ¹⁴	-
Lu	[Xe]4f ¹⁴ 5d ¹ 6s ²	[Xe]4f ¹⁴ 5d ¹ 6s ²	4f ¹⁴	-	-

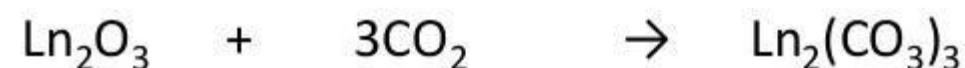
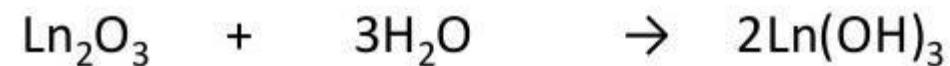
Chemical reactivity of Lanthanoids



lanthanoids (Ln)



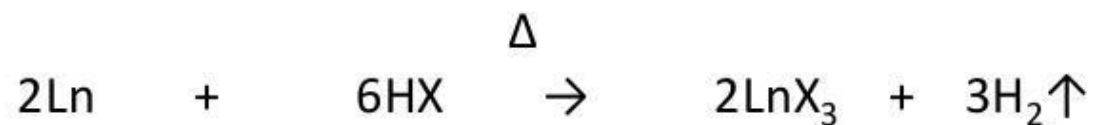
- The oxide Ln_2O_3 react with water to form insoluble hydroxides.



- $$2\text{Ln} + 3\text{H}_2\text{O} \rightarrow 2\text{Ln}(\text{OH})_3 + 3\text{H}_2$$

lanthanoid water Halide

- They liberate hydrogen from dilute acids.

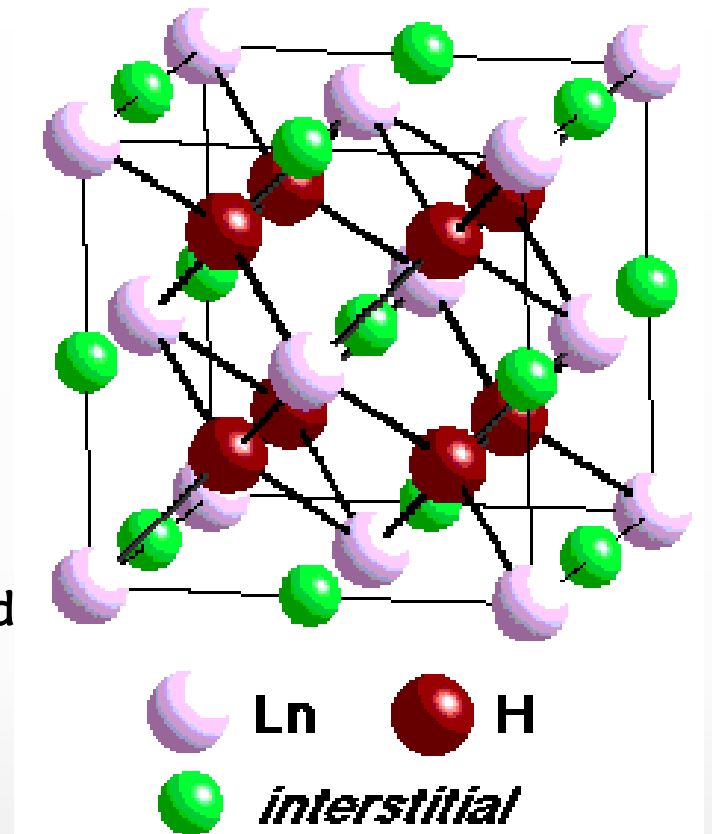


Lanthanide hydrides

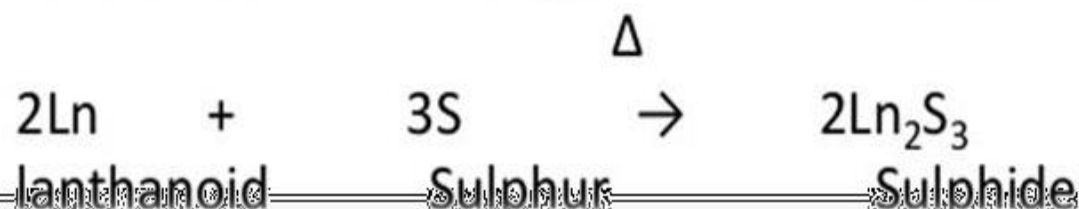
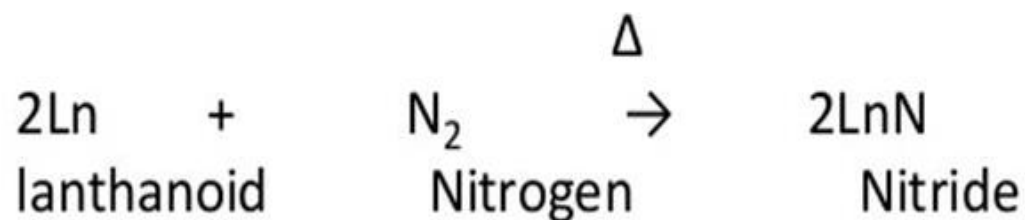
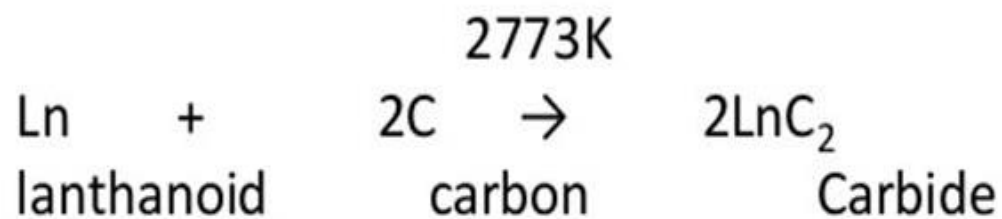
Preparation: Heat at 300-350°C, $\text{Ln} + \text{H}_2 \rightarrow \text{LnH}_2$

Properties of LnH_2

- black, reactive, highly conducting, fluorite structure
- Most thermodynamically stable of all binary metal hydrides
- Formulated as $\text{Ln}^{3+}(\text{H}^-)_2(\text{e}^-)$ with e^- delocalized in a metallic conduction band
- Further H can often be accommodated in interstitial sites, frequently non-stoichiometric.
- e.g. LuH_x where $x = 1.83-2.23$ & $2.78-3.00$
- High pressure on $(\text{H}_2 + \text{LnH}_3)$
- Reduced conductivity: salt-like $\text{Ln}^{3+}(\text{H}^-)_3$ except for Eu and Yb (the most stable LnII)



On being heated, these elements combine directly with non-metals, and form carbides with carbon, nitrides with nitrogen, sulphides with sulphur, and halides with halogens.



properties

- Silvery white soft metals, tarnish in air rapidly
- Hardness increases with increasing atomic number, samarium being steel hard.
- Good conductor of heat and electricity.
- Promethium - Radioactive

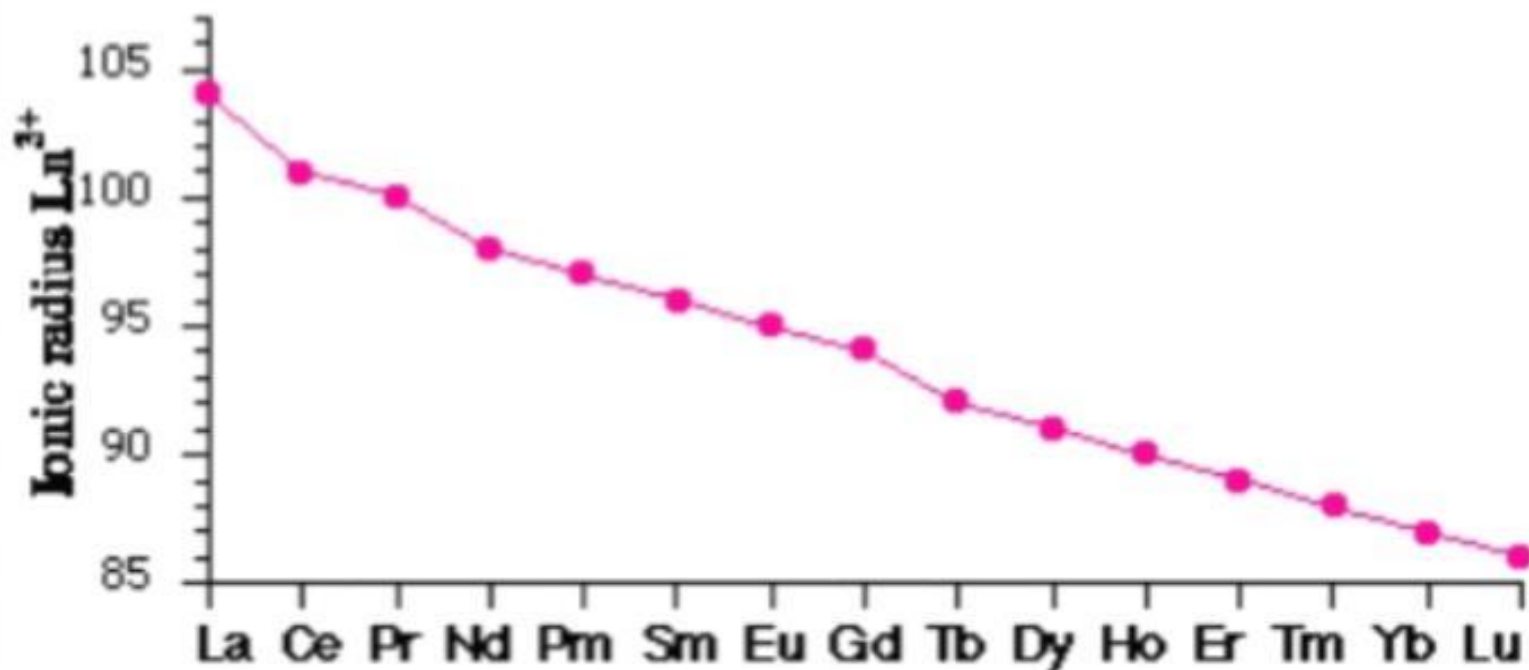
- LaC_2 reacts with water to form ethyne, C_2H_2 and a mixture of complex hydrocarbons.
- LaC_2 is a metallic conductor, in contrast to CaC_2 which is an insulator.
- The crystal structure of LaC_2 shows that it contains C_2 units with a C-C bond length of 130.3 pm, which is longer than the C-C bond length in calcium carbide, 119.2 pm, which is close to that of ethyne.
- The structure of LaC_2 can be described as $\text{La}^{3+}\text{C}_2^{2-}(\text{e}^-)$ where the electron enters the conduction band and antibonding orbitals on the C_2 anion, increasing the bond length.

LANTHANIDE CONTRACTION:

As the atomic number increases each succeeding element, contains one more electron in the 4f orbital and one proton in the nucleus. The 4f electrons are ineffective in screening 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.

* Lanthanides	Lanthanum	Cerium	Praseodymium	Neodymium	Promethium	Samarium	Europium	Gadolinium	Terbium	Dysprosium	Holmium	Erbium	Thulium	Ytterbium	Lutetium
	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

- The shielding effect of 4f is very smaller than d orbital as 4f Orbital is much diffuse in nature.



AS A RESULT IONIC RADII DECREASE

Consequences

I Among Lanthanides –

1. **Basicity** of ions- decreases from La^{3+} to Lu^{3+} so their oxides and hydroxides are less basic
2. As the atomic size decreases across the series the elements following lanthanides show change in their physical properties.
 - a) The ionisation potential increases
 - b) Metallic nature decreases
 - c) Electropositivity decreases
 - d) Electronegativity Increases
 - e) Tendency to form complexes increases

II Post Lanthanides –

i) **Occurrence of elements as pairs** – Due to similar size of 4d and 5d in a group, they have similar physical and chemical properties, they occur together in nature and their separation becomes very difficult.

Zr/Hf, Nb/Ta, Mo/W

ii) **Densities** – 5d elements have very high densities as down the group there is large increase in mass but no increase in volume.

III Occurrence of Yttrium along with heavier lanthanides –

yttrium has similar charge and size to Ho^{3+} & Er^{3+} hence it occurs with and separation is difficult.

3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB
21 Sc Scandium 44.955908 2-6-3-2	22 Ti Titanium 47.867 2-6-3-2	23 V Vanadium 50.9415 2-6-3-2	24 Cr Chromium 51.9961 2-6-3-2	25 Mn Manganese 54.938044 2-6-3-2	26 Fe Iron 55.845 2-6-3-2	27 Co Cobalt 58.933 2-6-3-2	28 Ni Nickel 58.693 2-6-3-2	29 Cu Copper 63.546 2-6-3-1	30 Zn Zinc 65.38 2-6-3-2
39 Y Yttrium 88.90584 2-6-3-1-2	40 Zr Zirconium 91.224 2-6-3-3-2	41 Nb Niobium 92.90637 2-6-3-3-1	42 Mo Molybdenum 95.95 2-6-3-3-1	43 Tc Technetium (98) 2-6-3-3-2	44 Ru Ruthenium 101.07 2-6-3-3-1	45 Rh Rhodium 102.91 2-6-3-3-1	46 Pd Palladium 106.42 2-6-3-3-1	47 Ag Silver 107.87 2-6-3-3-1	48 Cd Cadmium 112.40 2-6-3-3-2
57-71 Lanthanides	72 Hf Hafnium 178.49 2-6-3-3-2	73 Ta Tantalum 180.94788 2-6-3-3-2	74 W Tungsten 183.84 2-6-3-3-2	75 Re Rhenium 186.21 2-6-3-3-2	76 Os Osmium 190.23 2-6-3-3-2	77 Ir Iridium 192.22 2-6-3-3-2	78 Pt Platinum 195.08 2-6-3-3-1	79 Au Gold 196.97 2-6-3-3-1	80 Hg Mercury 200.59 2-6-3-3-2
89-103 Actinides	104 Rf Rutherfordium (261) 2-6-3-3-2-3-3-2	105 Db Dubnium (268) 2-6-3-3-3-2-3-2	106 Sg Seaborgium (266) 2-6-3-3-3-2-3-2	107 Bh Bohrium (270) 2-6-3-3-3-2-3-2	108 Hs Hassium (277) 2-6-3-3-3-2-3-2	109 Mt Meitnerium (276) 2-6-3-3-3-2-3-2	110 Ds Darmstadtium (285) 2-6-3-3-3-2-3-1	111 Rg Roentgenium (282) 2-6-3-3-3-2-3-1	112 Cn Copernicium (285) 2-6-3-3-3-2-3-2

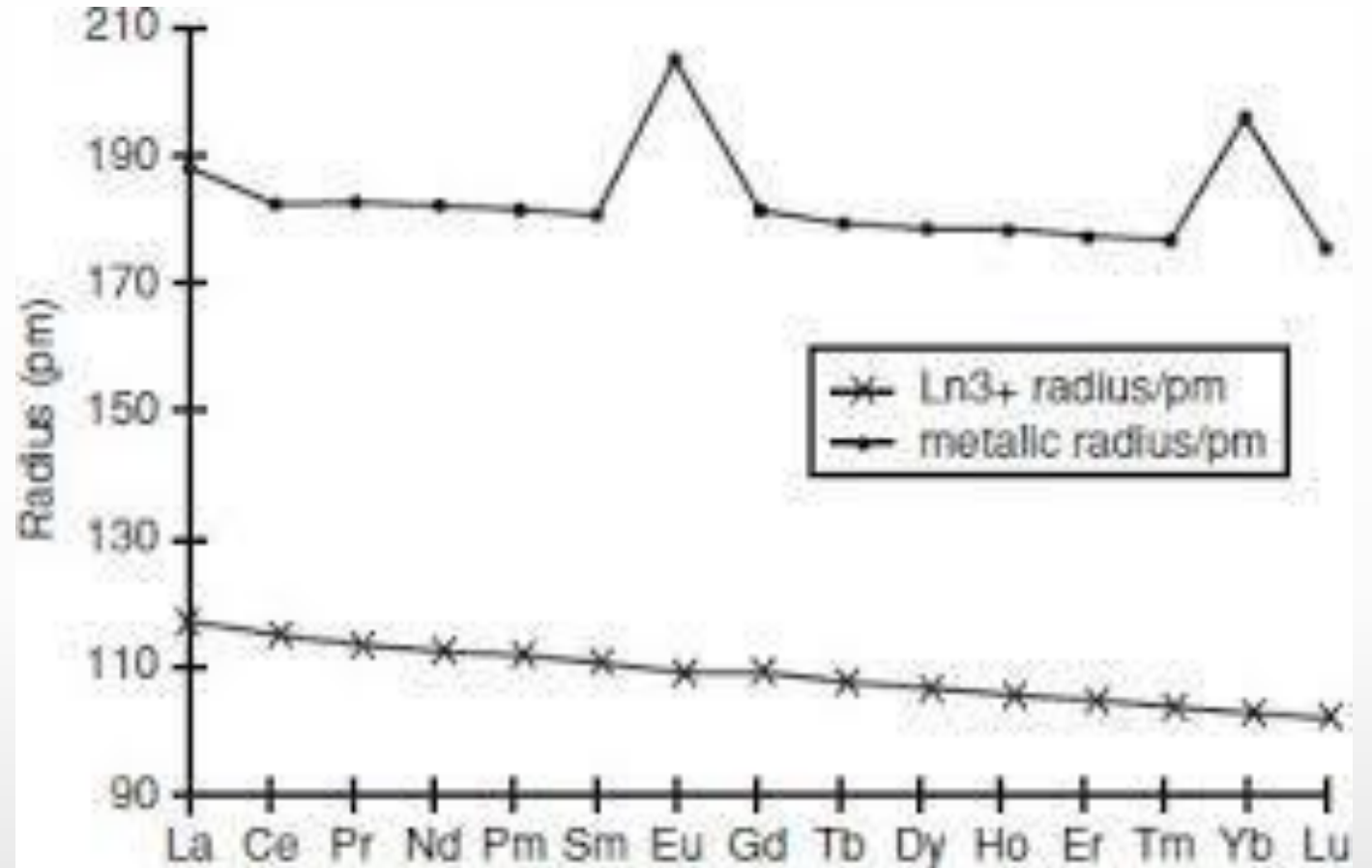
- The elements which follow the lanthanoids in the third transition series are known as post lanthanoids.
- The ionic radii of the elements which follow lanthanum (Hf, Ta, W, etc) are similar to that of the elements of the previous period.
- There is a normal increase in size from Sc to Y to La.

3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB
21 Sc Scandium 44.955908 2-8-9-2	22 Ti Titanium 47.867 2-8-10-2	23 V Vanadium 50.9415 2-8-10-2	24 Cr Chromium 51.9961 2-8-10-1	25 Mn Manganese 54.938044 2-8-10-2	26 Fe Iron 55.845 2-8-10-2	27 Co Cobalt 58.933 2-8-10-2	28 Ni Nickel 58.693 2-8-10-2	29 Cu Copper 63.546 2-8-10-1	30 Zn Zinc 65.38 2-8-10-2
39 Y Yttrium 88.90584 2-8-10-2	40 Zr Zirconium 91.224 2-8-10-2	41 Nb Niobium 92.90637 2-8-10-1	42 Mo Molybdenum 95.95 2-8-10-1	43 Tc Technetium (98) 2-8-10-2	44 Ru Ruthenium 101.07 2-8-10-1	45 Rh Rhodium 102.91 2-8-10-1	46 Pd Palladium 106.42 2-8-10-1	47 Ag Silver 107.87 2-8-10-1	48 Cd Cadmium 112.41 2-8-10-2
57-71 Lanthanides	72 Hf Hafnium 178.49 2-8-10-2	73 Ta Tantalum 180.94788 2-8-10-2	74 W Tungsten 183.84 2-8-10-2	75 Re Rhenium 186.21 2-8-10-2	76 Os Osmium 192.23 2-8-10-2	77 Ir Iridium 192.22 2-8-10-2	78 Pt Platinum 195.08 2-8-10-1	79 Au Gold 196.97 2-8-10-1	80 Hg Mercury 200.59 2-8-10-2
89-103 Actinides	104 Rf Rutherfordium (261) 2-8-10-2	105 Db Dubnium (268) 2-8-10-2	106 Sg Seaborgium (266) 2-8-10-2	107 Bh Bohrium (270) 2-8-10-2	108 Hs Hassium (277) 2-8-10-2	109 Mt Meitnerium (278) 2-8-10-2	110 Ds Darmstadtium (285) 2-8-10-1	111 Rg Roentgenium (282) 2-8-10-1	112 Cn Copernicium (285) 2-8-10-2

Variation of properties

Metallic radii

- Decreases with increase in atomic numbers (174-208 pm).
- Comparable with those of S-block elements.
- Fairly large size.
- Eu and Yb show very surprisingly irregular sizes because of repulsion between greater number of f- electrons.



Density

- Low densities (6.77 – 9.74 g/CC).
- Don't show definite trends with rise in atomic number.
- Eu and Yb have low values of density than expected.

Electronegativity values

- Range 1.0 – 1.15 (Allred and Rochow scale).
- Comparable with E.N. values of S-block elements.
- So, Ln compounds are expected to form ionic compounds.

Ionization Enthalpies

- Fairly low I. E
- First ionization enthalpy is around 600 kJ mol⁻¹, the second about 1200 kJ mol⁻¹ comparable with those of calcium.
- Due to low I. E, lanthanides have high electropositive character

Magnetic behaviour

❖ La^{3+} and Lu^{3+} do not contain any unpaired electrons, so they do not show paramagnetism. **All other tri positive ions of lanthanides are paramagnetic.**

❖ the 4f electrons are **deep inside** the ion and are well shielded from the quenching effect of the environment. The 4f-orbitals are **well shielded** from the surroundings by the overlying 5s and 5p-orbitals. As a result, the electric field of the ligands surrounding the ion **does not restrict the orbital motion of the electron**. So, in this case the observed paramagnetism is due to both factors – the electron spin and orbital motion.

- Paramagnetism.
- Magnetic properties have spin & orbit contributions (contrast "spin-only" of transition metals).
- Magnetic moments of Ln^{3+} ions are generally well-described from the coupling of spin and orbital angular momenta - Russell-Saunders Coupling Scheme.
- Spin orbit coupling constants are typically large (ca. 1000 cm^{-1}).
- Ligand field effects are very small (ca. 100 cm^{-1}).
 - only ground J-state is populated.
 - spin-orbit coupling \gg ligand field splittings.
 - magnetism is essentially independent of environment.

Magnetic moment of a J-state is expressed by the Landé formula:

$$\mu = g_J \sqrt{J(J+1)} \mu_B \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Ln³⁺ Magnetic Moments compared with Theory

Landé formula fits well with observed magnetic moments for all but Sm^{III} and Eu^{III}.

Moments of Sm^{III} and Eu^{III} are altered from the Landé expression by temperature-dependent population of low-lying excited J-state(s).

Uses of Ln³⁺ Magnetic Moments?

NMR Shift Reagents - paramagnetism of lanthanide ions is utilized to spread resonances in ¹H NMR of organic molecules that coordinate to lanthanides.

Magnetism & Spectra

Ln	Ln ³⁺ configuration	Ground State	No. of unpaired e-	Colour	$g_J\sqrt{J(J+1)}$	Observed μ_{eff}/μ_B
La	4f ⁰	¹ S ₀	0	colourless	0	0
Ce	4f ¹	⁴ F _{5/2}	1	colourless	2.54	2.3 - 2.5
Pr	4f ²	³ H ₄	2	green	3.58	3.4 - 3.6
Nd	4f ³	⁴ I _{9/2}	3	lilac	3.62	3.5 - 3.6
Pm	4f ⁴	⁵ I ₄	4	pink	2.68	-
Sm	4f ⁵	⁶ H _{5/2}	5	yellow	0.85	1.4 - 1.7
Eu	4f ⁶	⁷ F ₀	6	pale pink	0	3.3 - 3.5
Gd	4f ⁷	⁸ S _{7/2}	7	colourless	7.94	7.9 - 8.0
Tb	4f ⁸	⁷ F ₆	6	pale pink	9.72	9.5 - 9.8
Dy	4f ⁹	⁶ H _{15/2}	5	yellow	10.65	10.4 - 10.6
Ho	4f ¹⁰	⁵ I ₈	4	yellow	10.6	10.4 - 10.7
Er	4f ¹¹	⁴ I _{15/2}	3	rose-pink	9.58	9.4 - 9.6
Tm	4f ¹²	³ H ₆	2	pale green	7.56	7.1 - 7.6
Yb	4f ¹³	² F _{7/2}	1	colourless	4.54	4.3 - 4.9
Lu	4f ¹⁴	¹ S ₀	0	colourless	0	0

- For Sm³⁺ at room temperature, the first excited state and for Eu³⁺, the first excited state and even the second and third excited states are populated.
- In each of these ions, the J value is higher than that of the ground state and μ is expected to be greater than that of only the ground state.

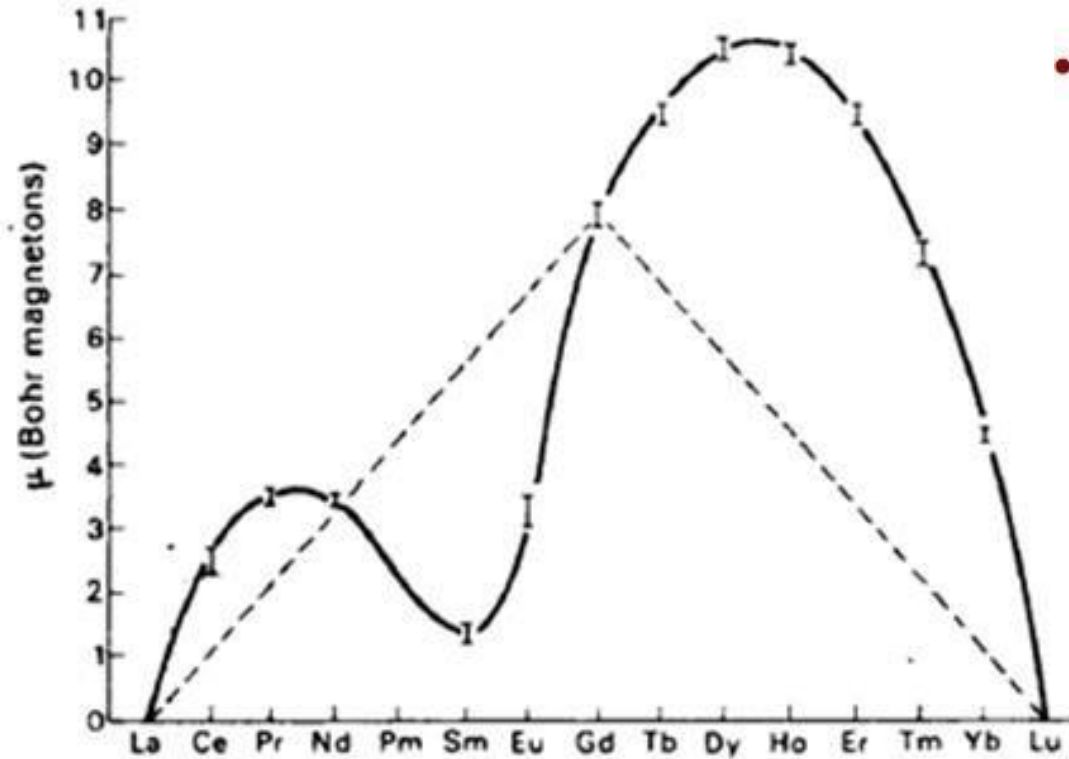


Figure Paramagnetic moments of Ln^{3+} lanthanide ions at 300 K. Spin-only values are shown as a broken line, and the spin plus orbital motion as solid lines.

- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{3+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic. The paramagnetism rises to the maximum in neodymium.

- La^{3+} is diamagnetic (due to f^0).
- Max value at Nd.
- Sudden drop to 1.47 for Sm.
- Increases again reaching max value for Dy and Ho.
- Touching zero at Lu (f^{14} electron).

Coloured ions

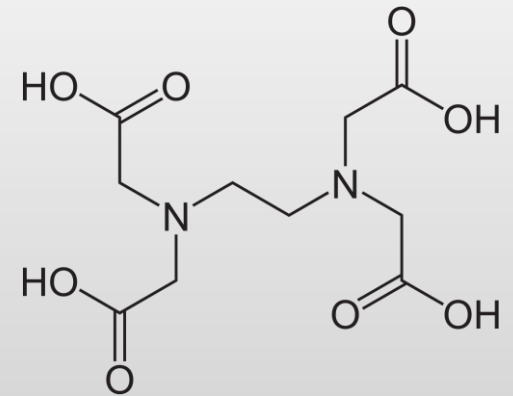
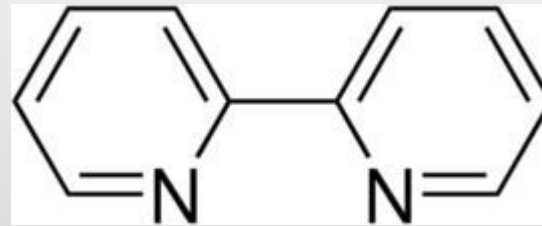
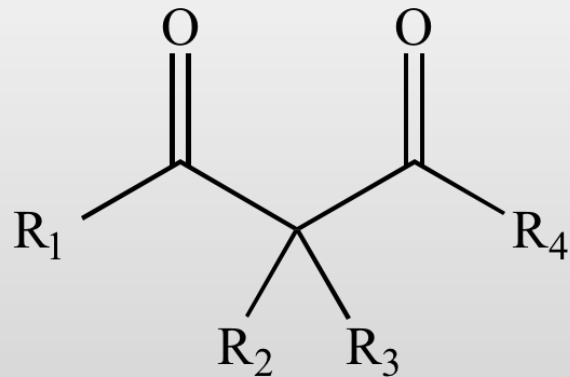
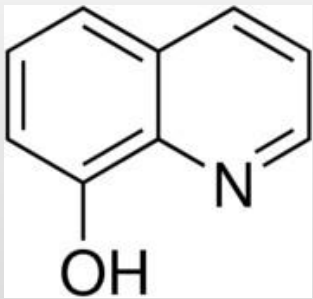
- Many of the lanthanoid ions are coloured in both solid and in solution due to **f – f transition** since they have **partially filled f – orbitals**.
- Absorption bands are narrow, probably because of the excitation within f level.
- La^{3+} and Lu^{3+} ions do not show any colour due to vacant and fully filled f- orbitals.
- The absorption spectra of the compounds of trivalent Ln ions show sharp line like bands (fainter color comparative to TMs) in the U.V., visible or near infrared regions.
- The bands are so sharp that they are very useful for characterizing the lanthanides and for their quantitative estimations.

Approximate colors of lanthanide ions in aqueous solution

Oxidation state	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
+2						Sm²⁺	Eu²⁺						Tm²⁺	Yb²⁺	
+3	La³⁺	Ce³⁺	Pr³⁺	Nd³⁺	Pm³⁺	Sm³⁺	Eu³⁺	Gd³⁺	Tb³⁺	Dy³⁺	Ho³⁺	Er³⁺	Tm³⁺	Yb³⁺	Lu³⁺
+4		Ce⁴⁺	Pr⁴⁺	Nd⁴⁺					Tb⁴⁺	Dy⁴⁺					

Lanthanides have poor tendency to form complexes

- Although the lanthanide ions have high charge (+3), yet the size of their ions is very large (charge/size = small).
- So, they have poor tendency to form complexes.
- They form complexes mainly with chelating agents (beta-diketone, EDTA, 2,2'-bipyridyl, and beta-hydroxy quinoline).
- Complex formation tendency and stability increases with increasing atomic number.
- This fact is utilized in the separation of lanthanides.



Chemistry of all lanthanides is almost identical

- They all have similar outer electronic configuration and display mainly +3 oxidation state in their compounds.
- Their similarity is much closer than that of ordinary transition elements because lanthanides differ mainly in the number of 4f electrons.
- 4f electrons are buried deep in the atoms.
- Due to L. C. there is very small difference in the size of all the 15 trivalent lanthanide ions.

Important uses of Lanthanides

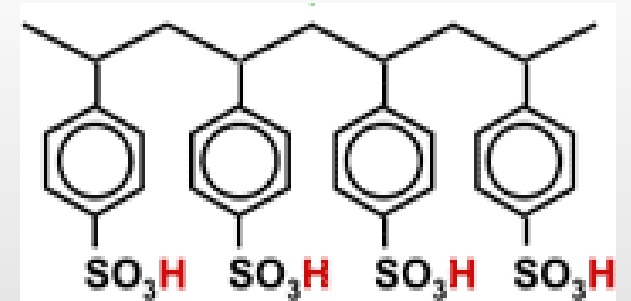
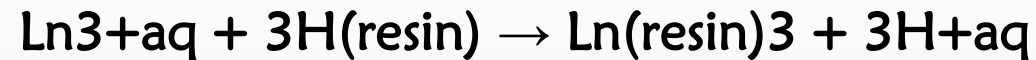
- Ce glass cuts off heat and UV light and so used in glare-reducing spectacles.
- Ce-Mg alloys are used in flashlight powders.
- Nd oxide dissolved in selenium oxychloride is one of the most powerful liquid lasers known so far.
- Ce salts are used in analysis, dyeing, lead accumulators, medicines and as catalyst.
- Ln elements and their compounds are being used in nuclear control, shielding and fluxing devices.
- Since lanthanides improve the workability of steel when heated, so alloys of lanthanides with Fe are well-known.
- $Gd_2(SO_4)_3 \cdot 7H_2O$ has been used to produce very low temperature.

SEPARATION OF LANTHANIDES:

Except promethium, they occur together in earth's crust in various forms and very difficult to separate from each other because all the lanthanides have the same size and charge (of +3 unit). The chemical properties of these elements which depend on the size and charge are, therefore, almost identical. Hence, their isolation from one another is quite difficult. However, the following methods have been used to separate them from one another.

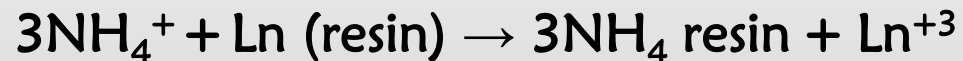
Separation of Ln: Ion exchange method

- This is the most rapid and most effective method for the isolation of individual lanthanide elements from the mixture. An aqueous solution of the mixture of lanthanide ions ($\text{Ln}^{3+}_{\text{aq}}$) is introduced into a column containing a synthetic cation exchange resin such as DOWAX-50. The resin is the sulphonated polystyrene containing SO_3H as the functional group. As the solution of mixture moves through the column, $\text{Ln}^{3+}_{\text{aq}}$ ions replace H^+ ions of the resin and get themselves fixed on it:



sulphonated polystyrene

- The bonding of the lanthanide ion to the resin depends on its size, i. e, the smaller the size of the lanthanide ion, the more firmly it is bound to the resin and vice versa. Since lanthanide ions are hydrated, therefore size of the hydrated ions should be considered for binding purpose. Hydration of the ions depends upon size i. e, smaller the size of the ion greater will be the hydration. Therefore in case of lanthanide ions, the smallest lanthanide ion, namely will be the most heavily hydrated. Thus it will have the maximum size and therefore the least firmly bound to the resin while reverse will be the case with La+3 which will be the most firmly bound to the resin
- A solution containing several lanthanide ions is dropped slowly down a column of synthetic ion exchange resin so that the lanthanide ions are bound less firmly to the resin in the order La+3 to Lu+3. They are then eluted from the column by using a solution containing citric acid and ammonium citrate. For the ammonium ions elute the metal ions from the resin as:

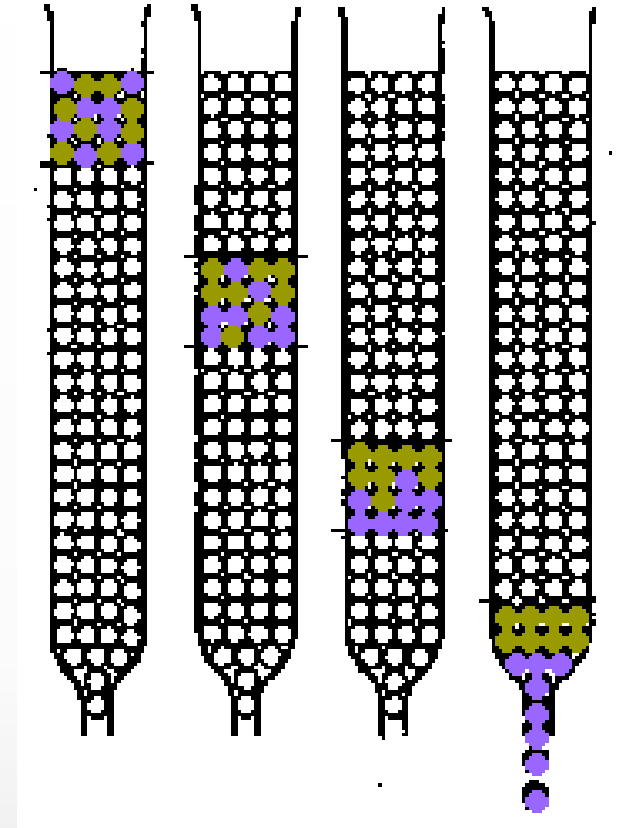


The metal ions then form a complex with the citrate ions.



complex

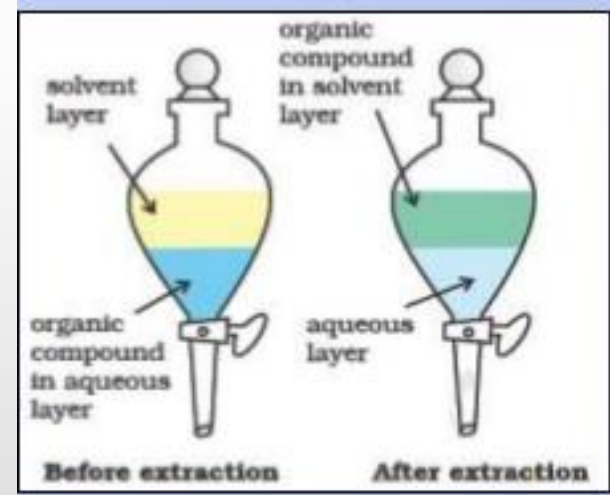
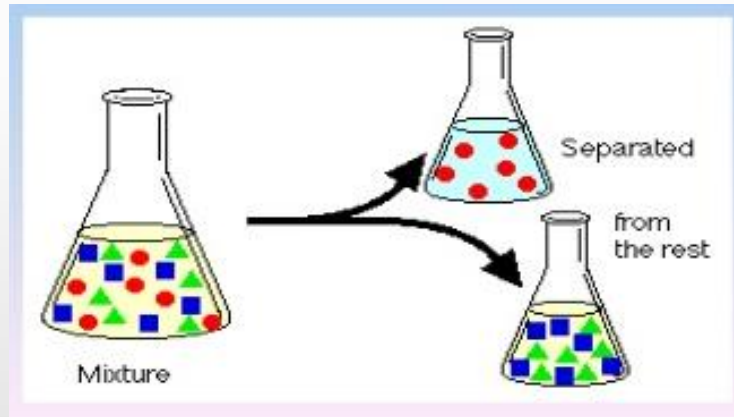
Since Lu^{+3} is the least firmly bound to resin therefore on elution, Lu citrate complex is obtained first from the bottom of the column while La citrate complex emerges last of all from the bottom of the column. Complexing agents such as EDTA, amino carboxylic acids and hydroxy carboxylic acids have also been found to be convenient elutants.



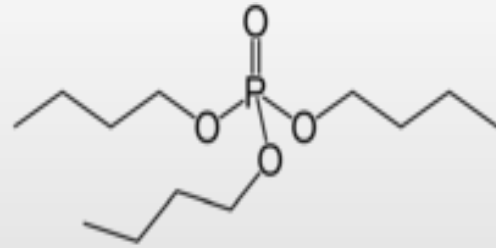
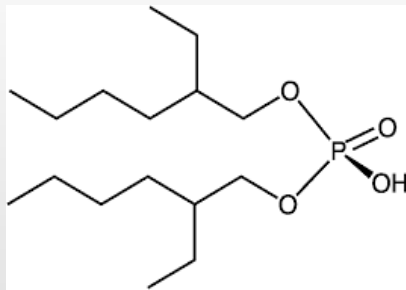
Solvent extraction method: Separation of Lanthanides

What is Solvent Extraction ?

Solvent Extraction, also known as liquid-liquid extraction, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent.



This method is based on the **difference in partition co-efficients** of lanthanide salts between water and organic solvents. The solvents employed in this method of extraction of the lanthanides are usually **tri n-butyl phosphate (TBP) and di (2-ethylhexy) phosphoric acid**. For eg. $Gd(NO_3)_3$ can be separated from $La(NO_3)_3$ by continuous extraction with water from a solution of these salts in TBP .



Decreases in ionic radius will increase complexation.

Some CONTRASTS between Lanthanides & Pre-Transition & Transition Metals

<i>Pre-Transition Metals</i>	<i>Lanthanides</i>	<i>Transition Metals</i>
Essentially Monovalent - show Group (n+) oxidation state	Essentially Monovalent (+3). +2/+4 for certain configs	Show Variable Valence (extensive redox chemistry) control by environment - ligands, pH etc...
Periodic trends dominated by (effective nuclear) charge at noble gas config (i.e. on group valence).	Lanthanide Contraction of Ln ³⁺ .	Size changes of M ⁿ⁺ less marked.
Similar Properties for a given group (differentiated by size).	Similar Properties (differentiated by size).	Substantial Gradation in Properties.
widespread on earth.	common mineralogy	diverse mineralogy
No Ligand Field Effects.	Insignificant Ligand Field Effects.	Substantial Ligand Field Effects.
Always 'hard' (O, Hal, N donors) (preferably -vely charged)	Always 'hard' (O, X, N donors) (preferably -vely charged)	Later (increasingly from Fe-Cu)/heavier metals may show a 'soft' side.
'Ionic' or 'Covalent' Organometallics	'Ionic' Organometallics.	'Covalent' Organometallics.
No Ligand Effects.	Paucity of Ligand Effects.	π -Acceptor Ligands - Extensive Chemistry.
Poor Coordination Properties (C.N. determined by size).	High Coordination Numbers (C.N. determined by size).	Extensive Coordination C.N. = 6 is typical maximum (but many exceptions).
Flexibility in Geometry.	Flexibility in Geometry.	Fixed (by Ligand Field effects) Geometries.
No Magnetism from the metal ions - noble gas configurations of ions	Free Ion-like Magnetism ground state magnetism	Orbital Magnetism 'Quenched' by Ligand Fields. excited J-states populated.
'Ionic' compound formulations → large HOMO-LUMO gaps → UV CT spectra	Weak, Narrow Optical Spectra. Forbidden, unassisted transitions.	Stronger, Broader Optical Spectra. Forbidden transitions. Vibronically-assisted.

Actinoids

- 7 period and actinide series.
- Electron enter in 5f orbital.
- Many physical and chemical property are similar to actinium(actinoids).
- Second inner transition element.
- Outermost and penultimate shell remain the same.
- General E.C $5f^{1-10} 6d^{0-1} 7s^2$
 - First 4 member occur in nature.
 - Others are made artificially.
 - All are toxic to humans.

89 Ac actinium [227]	90 Th thorium 232.038 06(2)	91 Pa protactinium 231.035 88(2)	92 U uranium 238.028 91(3)	93 Np neptunium [237]	94 Pu plutonium [244]	95 Am americum [243]
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96 Cm curium [247]	97 Bk berkelium [247]	98 Cf californium [251]	99 Es einsteinium [252]	100 Fm fermium [257]	101 Md mendelevium [258]	102 No nobelium [259]	103 Lr lawrencium [262]
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Representative Elements

← s-block →

Transition Elements

d-block

← p-block →

Noble gases 18

Periods: 1, 2, 3, 4, 5, 6, 7

Groups: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18

Inner Transition Elements

f-block

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

Electronic configuration

- Ac (89)-
 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6 6d^1 7s^2$.
- [Rn]- 86
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6$
- Ac electronic configuration is
- [Rn] $6d^1 7s^2$ or [Rn] $5f^0 6d^1 7s^2$
- 6d and 7s electron is same only 5f electron change by increasing order. Th(90)- [Rn] $5f^1, \dots, 5f^{10}$.

Z	Name	Symbol	Electronic configuration outside the [Xe] core		Metallic radius (pm)	Ionic radius M^{3+} (pm)	$E^*(V)$ M^{3+}/M	Color of Ln^{3+}
			An	An^{3+}				
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$	-	112	- 2.6	Colourless
90	Thorium	Tc	$6d^2 7s^2$	$5f^1$	179	-	-	-
91	Protactinium	Pa	$5f^2 6d^1 7s^2$	$5f^2$	163	104	- 1.95	Colourless
92	Uranium	U	$5f^3 6d^1 7s^2$	$5f^3$	156	103	- 1.80	Red Brown
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	155	101	- 1.86	Purplish
94	Plutonium	Pu	$5f^6 7s^2$	$5f^5$	155	100	- 2.03	Blue Violet
95	Americium	Am	$5f^7 7s^2$	$5f^6$	159	98	- 2.38	Pink
96	Curium	Cm	$5f^7 6d^1 7s^2$	$5f^7$	173	97	-	Pale Yellow
97	Berkelium	Bk	$5f^9 7s^2$	$5f^8$	174	96	-	-
99	Californium	Cf	$5f^{10} 7s^2$	$5f^9$	170	95	-	-
98	Einsteinium	Es	$5f^{11} 7s^2$	$5f^{10}$	186 ± 2	-	-	-
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	186 ± 2	-	-	-
101	Mendelevium	Md	$5f^{13} 7s^2$	$5f^{12}$	-	-	-	-
102	Nobelium	No	$5f^{14} 7s^2$	$5f^{13}$	-	-	-	-
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	-	-	-	-

As there is not much difference between 5f and 6d, it becomes difficult to know whether the electron has entered 5f or 6d. This makes predicting electronic configuration difficult.

- The ground state electronic configuration of actinium, $[\text{Rn}]6d^17s^2$ is identical to that of lanthanum and certainly the two elements possess alike chemical properties.
- The difference in energy between 5f and 6d orbitals in the starting of the actinide series is less than that between the 4f and 5d orbitals for the lanthanides.
- Thus, both 5f and 6d orbitals are comprised in accommodating successive electrons.
- Therefore the filling of 5f orbitals in actinides is not quite so regular as the filling of 4f orbitals in case of the lanthanides.
- By the time plutonium and following members of the series are reached, the 5f orbitals seem evidently to be of lower energy than the 6d orbitals, and therefore the electrons preferably fill the former.

Actinides show higher oxidation states than Lanthanides

Oxidation state

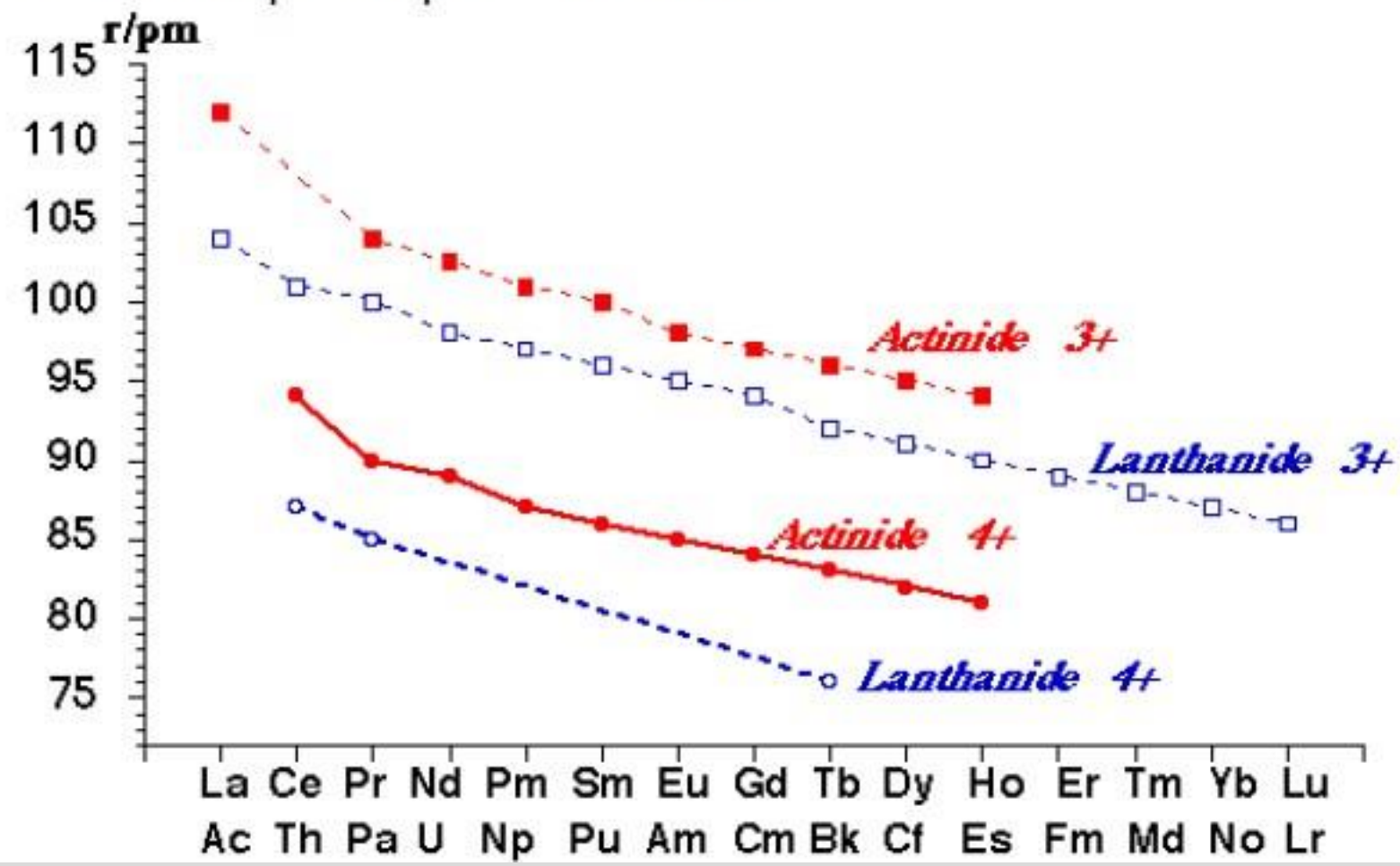
Name	Oxidation states
Actinium	+3
Thorium	+3, +4
Protactinium	+3, +4, +5
Uranium	+3, +4, +5, +6
Neptunium	+3, +4, +5, +6, +7
Plutonium	+3, +4, +5, +6, +7
Americium	+2, +3, +4, +5, +6
Curium	+3, +4
Berkelium	+3, +4
Californium	+2, +3
Einsteinium	+2, +3
Fermium	+2, +3
Mendelevium	+2, +3
Nobelium	+2, +3
Lawrencium	+3

- Up to Uranium, stable oxidation states of the elements is the one involving all the valency electrons.
- Neptunium forms the +7 state using all the valency electrons but this is oxidizing and the most stable state is +5.
- Plutonium also shows states up to +7 and Americium up to +6 but the most stable state drops to Pu (+4) and Am (+3).
- Berkelium in +4 state is strongly oxidizing but is more stable than curium and americium in +4 state due to f7 configuration.
- Similarly, nobelium is markedly stable in +2 state due to its f14 configuration.

Actinide contraction

- The contraction is caused due to imperfect shielding of one 5f electron by another in the same shell.
- As we move along the actinide series, the nuclear charge and the number of 5f electrons increase one unit by each step.
- Due to imperfect shielding (shape of f orbitals are very much diffused) the effective nuclear charge increases which causes contraction in the size of electron cloud.
- In actinides contraction there are bigger jumps in contraction between the consecutive elements as compared to lanthanides.
- Lesser shielding of 5f electrons compared to 4f electrons.

- Ionic Radii of ions show a clear "Actinide Contraction"
- ✚ Actinide 3+ or 4+ ions with similar radii to their Lanthanide counterparts show similarities in properties that depend upon ionic radius

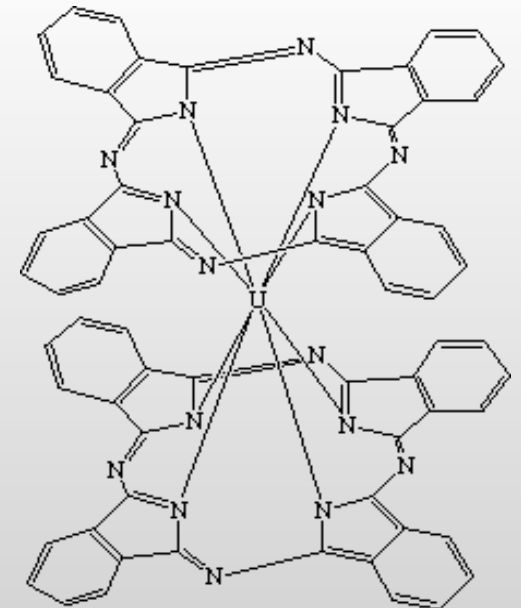
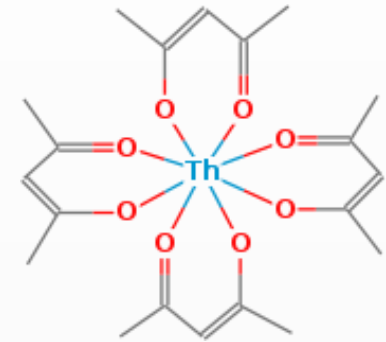
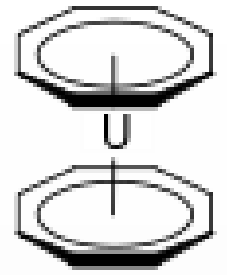


Variation in properties

- M. P. and B. P. – There is no regular trend in these values.
- Density increases from left to right.
- Magnetic properties: Smaller than the theoretically predicted values due to quenching of orbital contraction.
- Reducing power (E° values): All of them have relatively high E° values (about 2 volts).
- Reactivity: Very reactive metals. The reactions of metals with oxygen, halogens and acids resemble those with lanthanides.
- Colored ions: Color depends upon the number of 5f electrons. Color is exhibited due to f-f transition.

Actinides have greater tendency to form complexes than lanthanides

- Small and highly charged M^{4+} ions exhibit greater tendency towards complex formation, e.g. Pu^{4+} forms very strong anion complexes.
- Most actinide halides form adducts with alkali metal halides. $ThCl_4$ forms the complexes $MThCl_5$, M_2ThCl_6 , M_3ThCl_7 .
- With pyridine, $ThCl_4$ as well as $ThBr_4$ form monopyridine complexes.
- Also form complexes with acetylacetonate, oxine (8-hydroxyquinoline), EDTA, such as tetrakis-(acetylacetonato)thorium, $Th(acac)_4$ etc.
- UO_2 forms rather unstable complex with EDTA as compared to lanthanides.



Chemical properties

- ✓ All the actinides are not stable with respect to the radioactive disintegration, although the half-lives of the richest isotopes of thorium and uranium are so long that for numerous purposes their radioactivity can be neglected.
- ✓ Like lanthanides, actinides are as well electropositive and reactive metals.
- ✓ They react with water, oxygen, hydrogen, halogens and acids. Their hydrides are non-stoichiometric having ideal formulae MH_2 and MH_3 .
- ✓ The metals as well react with most of the non-metals particularly whenever heated.

General Observations (comparisons with Lanthanides)

- Electronic Configurations of Actinides are not always easy to confirm.
 - ✚ Atomic spectra of heavy elements are very difficult to interpret in terms of configuration. Competition between $5f^n 7s^2$ and $5f^{n-1} 6d 7s^2$ configurations is of interest.
 - ✚ For early actinides promotion $5f \rightarrow 6d$ occurs to provide more bonding electrons. Much easier than corresponding $4f \rightarrow 5d$ promotion in lanthanides.
 - ✚ Second half of actinide series resemble lanthanides more closely.
- 5f orbitals have greater extension wrt 7s and 7p than do 4f relative to 6s and 6p orbitals, e.g. ESR evidence for covalent bonding contribution in UF_3 , but not in NdF_3 .
- 5f / 6d / 7s / 7p orbitals are of comparable energies over a range of atomic numbers, especially U–Am.

Electronic Spectra

- ⚡ Narrow bands (compared to transition metal spectra).
- ⚡ Relatively uninfluenced by ligand field effects.
- ⚡ Intensities are ca. 10 x those of lanthanide bands.
- ⚡ Complex to interpret.

Magnetic Properties

- ⚡ Hard to interpret.
- ⚡ Spin-orbit coupling is large & Russell-Saunders (L.S) Coupling scheme doesn't work.
- ⚡ Ligand field effects are expected where 5f orbitals are involved in bonding.

- The magnetic properties of actinide ions are more complex than those of the lanthanide ions.
- 5f electrons are closer to the surface of the atom and is simply affected by the chemical environment; however not to the similar extent as do the d electrons.
- The less sharply stated distinctions between the 5f and 6d electrons as compared by 4f and 5d electrons.

Similarities

- Both the series show a +3 oxidation state.
- In both the series the f-orbitals are filled gradually.
- Ionic radius of the elements in both the series decreases with the increase in atomic number.
- The electronegativity of all the elements in both the series is low and are said to be highly reactive.
- The nitrates, per chlorates and sulphates of all the elements are soluble while the hydroxides, fluorides and carbonates are insoluble.

Lanthanides		Actinides	
i)	Binding energies of 4f electrons are higher.	i)	Binding energies of 5f electrons are lower.
ii)	Maximum oxidation state exhibited by lanthanides is +4 e.g. Ce^{4+}	ii)	Due to lower binding energies they show higher oxidation states such as +4, +5 and +6. Uranium exhibits +6 oxidation state in UF_6 and UO_2Cl_2
iii)	4f electrons have greater shielding effect.	iii)	5f electrons have poor shielding effect.
iv)	Most of their ions are colourless.	iv)	Most of their ions are coloured U^{3+} (red), U^{4+} (green) and UO_2^{2+} (yellow)
v)	They are paramagnetic but magnetic properties can be easily explained.	v)	They are also paramagnetic but their magnetic properties are very difficult to interpret.
vi)	They do not form complexes easily.	vi)	They have much greater tendency to form complexes.
vii)	Except promethium, they are non-radioactive.	vii)	All of them are radioactive.
viii)	Their compounds are less basic.	viii)	Their compounds are more basic.
ix)	They do not form oxocations.	ix)	They form oxocations such as UO_2^{2+} , UO^+ , NpO_2^+ , PuO_2^+ .

Magnetism & Spectra

Ln	Ln ³⁺ configuration	Ground State	No. of unpaired e-	Colour	$g_J \sqrt{J(J+1)}$	Observed μ_{eff}/μ_B
La	4f ⁰	¹ S ₀	0	colourless	0	0
Ce	4f ¹	⁴ F _{5/2}	1	colourless	2.54	2.3 - 2.5
Pr	4f ²	³ H ₄	2	green	3.58	3.4 - 3.6
Nd	4f ³	⁴ I _{9/2}	3	lilac	3.62	3.5 - 3.6
Pm	4f ⁴	⁵ I ₄	4	pink	2.68	-
Sm	4f ⁵	⁶ H _{5/2}	5	yellow	0.85	1.4 - 1.7
Eu	4f ⁶	⁷ F ₀	6	pale pink	0	3.3 - 3.5
Gd	4f ⁷	⁸ S _{7/2}	7	colourless	7.94	7.9 - 8.0
Tb	4f ⁸	⁷ F ₆	6	pale pink	9.72	9.5 - 9.8
Dy	4f ⁹	⁶ H _{15/2}	5	yellow	10.65	10.4 - 10.6
Ho	4f ¹⁰	⁵ I ₈	4	yellow	10.6	10.4 - 10.7
Er	4f ¹¹	⁴ I _{15/2}	3	rose-pink	9.58	9.4 - 9.6
Tm	4f ¹²	³ H ₆	2	pale green	7.56	7.1 - 7.6
Yb	4f ¹³	² F _{7/2}	1	colourless	4.54	4.3 - 4.9
Lu	4f ¹⁴	¹ S ₀	0	colourless	0	0

Thank You