F-Block.

Lanthenides

Lanthanum	La	$5d^1 6s^2$	Tb	$4f^9 5d^0 6s^2$	Terbium
Cerium	Ce	$4f^1 5d^1 6s^2$ or $4f^2 5d^0 6s^2$	Dy	$4f^{10} 5d^0 6s^2$	Dysprosium
raseodymium	Pr	$4f^2 5d^1 6s^2$ or $4f^3 5d^0 6s^2$	Ho	$4f^{11} 5d^0 6s^2$	Holmium
eodymium	Nd	$4f^4 5d^0 6s^2$	Er	$4f^{12} 5d^0 6s^2$	Erbium
romethium	Pm	$4f^5 5d^0 6s^2$	Tm	$4f^{13} 5d^0 6s^2$	Thulium
amarium	Sm	$4f^6 5d^0 6s^2$	Yb	$4f^{14} 5d^0 6s^2$	Ytterbium
uropium	Eu	$4f^7 5d^0 6s^2$	Lu	$4f^{14} 5d^1 6s^2$	Lutetium
dolimium	Gd	$4f^7 5d^1 6s^2$			

" College Party never provide simple Europian Girls That Drink eavily Even Though you Look. "

- Most common O.S. → +3.

La	f^0	Tb	f^8
Ce	f^1	Dy	f^9
Pr	f^2	Ho	f^{10}
Nd	f^3	Er	f^{11}
Pm	f^4	Tm	f^{12}
Sm	f^5	Yb	f^{13}
Eu	f^6	Lu	f^{14}
Gd	f^7		

→ Ce exist in both +3 as well as in +4. Because in +4 O.S., its electronic confi. becomes zero. i.e. stable one.

→ Tb also exist in +4 O.S because of stable one confi.

→ Eu → (+2 most stable) i.e. $4f^7$

→ Yb → Yb^{+2} $4f^{14}$

Colour f^0 & f^{14} don't show colour because of no unpaired electron. f^7 also don't show becoz it goes in opposite spin.

La	Colourless (study on)	Sm	Coloured	Ho	Coloured
Ce	Colourless	Eu	〃	Er	〃
Pr	coloured	Gd	Colourless	Tm	〃
Nd	〃	Tb	Coloured	Yb	colourless
Pm	〃	Dy	〃	Lu	〃

→ Because Ce do not remain in +3, O.S and goes to +4, i no unpaired $\bar{e}$ (f^1 → U.V. region, no colour)

→ Yb → similar to Ce.

⇒ (n) & (n−10) show same properties ∵ term symbols r sa

Magnetic Properties.

$$\mu_{total} = \mu_{spin} + \mu_{orbital}$$

$$\mu = g\sqrt{J(J+1)}$$

Lande's factor $g = \dfrac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$; $g = 1 + \dfrac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

Term symbols.

$$f^2 \quad \begin{array}{|c|c|c|c|c|c|c|} \multicolumn{1}{c}{+3} & \multicolumn{1}{c}{+2} & \multicolumn{1}{c}{+1} & \multicolumn{1}{c}{0} & \multicolumn{1}{c}{-1} & \multicolumn{1}{c}{-2} & \multicolumn{1}{c}{-3} \\ \hline 1 & 1 & & & & & \\ \hline \end{array}$$

$+3+2 = +5 = \textcircled{H}$

$\frac{1}{2} + \frac{1}{2} = 1$; ⇒ $2S+1 = 2\times1+1 = 3$

$J = |L+S| — |L-S|$
$|5+1| — |5-1| = 6, 5, 4$

∴ Ground state $\boxed{^3H_4}$

Magnetic moment for it is.

$$\mu = g\sqrt{J(J+1)}$$

$J = 4, S = 1, L = 5$

$$g = 1 + \frac{4(4+1) + 1(1+1) - 5(5+1)}{2\times4(4+1)} = 1 + \frac{20+2-30}{40}$$

$$g = 1 - \frac{8}{40} = \frac{40-8}{40} = \frac{32}{40} = \frac{4}{5}$$

$$\mu = \frac{4}{5}\sqrt{20} = \frac{4}{5}\times2\times2.2 = 3.6$$

$$\boxed{\mu = 3.6}$$

3.52

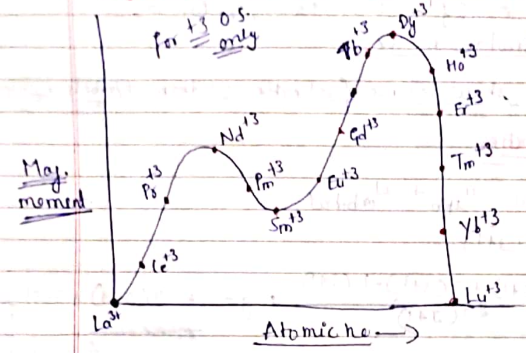
3.6

$2\times5\times2$

$2\sqrt{5}$

Imp.

Magnetic moment values Vs Atomic No.

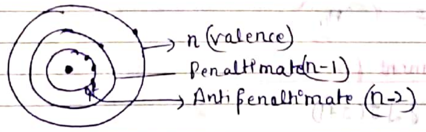


→ Here magnetic moment depend on g factor and g factor have -ve value and that -ve electronic mag. moment. [Not acc. to no. of $\bar{e}$ (f) ~~[illegible]~~ and hence mag. moment increase]

$Dy^{+3} \rightarrow f^9 \rightarrow$ maximum.

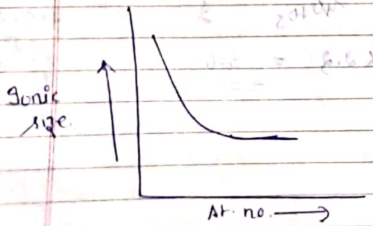
Ionic radii

Lanthenide contraction.



e^- goes to antipenaltimate, i.e. goes to 4f, hence shielding poor, so Z-eff ↑es, so size ↓es

↓
∵ f-diffused shape



Orbitals.

$f_{x^3}, f_{y^3}, f_{z^3}, f_{x^2(y-z)}, f_{y^2(z-x)}$, $f_{z^2(x-y)}, f_{xyz}$,

7-orbitals

Important points about Lanthenides.

(I) Pm ⇒ radioactive, others are non-radioactive

(II) +3 oxidation state is common.

∵ $\boxed{IE_1 + IE_2 + IE_3 \text{ is less.}}$

and also hydration energy is maximum for +3 oxidation state. Also Lattice is maximum for +3 O.S.

(IV) ~~to~~ High -ve value for +3 O.S. (reduction potential.)
-2.52 to -2.25 from La to Lu.

Liberates H^+ from mineral acids.

(V) Ce^{+4} is good oxidising agent.

$$\boxed{Ce^{4+} + \bar{e} \longrightarrow Ce^{3+}}$$

(VI) Reducing agent $\boxed{Eu^{2+} \longrightarrow Eu^{3+} + \bar{e}}$
⇓
more stable.

(V) Both Ce and Eu can be separated easily from the rest of Lanthenides due to their diff. chem behaviour

Ce Extraction.

Ce	Ce
+3	+4
→ more size	→ less size
→ more basic.	→ ~~more~~ less basic
→ less acidic →	more acidic.

$$\underset{\text{acidic}}{Ce^{4+}} + 4H_2O \longrightarrow \underset{\text{ppt.}}{Ce(OH)_4} + 4H^+$$

→ Easily decomposes H_2O and complexes $\bar{c}$ $\bar{O}H$ and easily separates out as $Ce(OH)_4$ ppt.

Ce^{4+} being less basic than rest of the Lanthenides undergoes hydrolysis easily hence Ce^{3+} oxidized by $KMnO_4$ or bleeching powder to Ce^{4+} which can ppt as basic salt or hydroxides.

⇒ Lanthenides have weak tendency to form complex because of less ionic potential due to large size.

⇒ It forms complexes c̄ chelating ligands and do not form with π-bonding ligands.
∵ 4f are smaller inside and are deeper so can not interact c̄ the π* antibonding orbital of π-acceptor ligand. Hense there will be no backbonding hense leading to unstability.

Ore→ Monazite sand. which contains the mixture of phosphate of Lanthenides, thorium and zirconium.
All procedure — self.

Solⁿ of Lanthenides can be separated by cation exchange method. They are separated by coloumn chromatography by the use of Dowek-50.

1) Dowek 50 ⇒ It is a reagent having sulphonic acid as functional group ~~HSO_3~~ $(-SO_3H)$

1) $$\underset{(aq)}{Ln^{3+}} + \underset{\substack{\downarrow \\ \text{from sulphonic acid}}}{H\text{-Resin}} \rightleftharpoons Ln\text{-}(Resin)_3 + 3H^+(aq)$$

Metal ions are eluted from column in a selective manner. The eluting agent is a complexing agent.
eg Buffer solⁿ of citric acid or ammonium citrate (pH 2.8–3.4)
or a dilute solution of $(NH_4)_3(H.EDTA)$ at (pH–8)

2) $$Ln(Resin)_3 + 3H^+(aq) + (H.EDTA)^{3-} \rightleftharpoons 3H(Resin) + Ln[H.EDTA]$$

As the EDTA runs down the column, the Lanthenide ions forms complexes alternatively c̄ resins and EDTA solⁿ many times.
The smaller Lanthenide ions such as Lu^{3+} forms stronger complexes c̄ EDTA than larger ions. Hense smaller and heavier ions are eluted from the column first.

⇒ Separation order.

$Lu^{3+} > Yb^{3+} > Tm^{3+} > Er^{3+} > Ho^{3+} > Dy^{3+} > Tb^{3+} > Gd^{3+} > Eu^{3+} > Sm^{3+} > Pm^{3+} > Nd^{3+} > Pr^{3+} > Ce^{3+} > La^{3+}$.

Consequences of Lanthenide contraction.
① size of 4d-and 5D series is almost same.
② Density of 5d series is high.
③ strongest complexes of Lu
④ Hardness, mpt., b.pt. of elt. ↑es from Ce – Lu due to ↓es in size.

General Rxns.

Lanthenides.

$$\xrightarrow{H_2O} Ln(OH)_3 + H_2$$
$$\xrightarrow[H_2O]{CO_2} Ln_2(CO_3)_3 + H_2$$
$$\xrightarrow[\Delta]{H_2} LnH_2, LnH_3$$
$$\xrightarrow[\Delta]{X_2} LnX_3$$
$$\xrightarrow{N_2} LnN$$
$$\xrightarrow{O_2} Ln_2O_3 \quad \text{Exception} \; (\overset{+4}{CeO_2})$$
$$\xrightarrow[N_2, O_2]{air} Ln_2O_3 + LnN$$

⇒ Alloys

Misch metal : Ce La Fe Other
↓ 50% 40% 7% 3%

⇒ Used to improve the strength and work ability of the steel.

Ln_2O_3 ⇒ crook's lense.

$Ce(SO_4)_2$ ⇒ volumetric analysis as oxidizing agent

β-diketon Complexes of Eu^{3+} and Pr^{3+} dissolve in organic solvent and used as shift reagent in NMR

Comman Coordination no. ⇒ 7, 8, 9.

The upper coordination no i.e. 10 & 12 are possible c̄ larger Lanthenides and small chelating ligands NO_3^- and SO_4^{2-}

e.g. Ce^{4+}

Coordination no. is governed by ligand's steric factors and not by crystal field effect.

232 90
237 93
236 92
235 92
208 82 58 52
209 83 59 51
206 82 58 51
207 82

Actinides

+3

Actium	89 Ac	$6d^1 7s^2$	$5f^0$
Thorium	90 Th	$6d^2 7s^2$	f^1
(Protactanium)	91 Pa	(~~Prota~~ $5f^2 6d^1 7s^2$	f^2
Uranium	92 U	$5f^3 6d^1 7s^2$	f^3
Nephunium	93 Np	$5f^4 6d^1 7s^2$	f^4
Plutonium	94 Pu	$5f^6 6d^0 7s^2$	f^5
	95 Am	$5f^7 6d^0 7s^2$	f^6
	96 Cm	$5f^7 6d^1 7s^2$	f^7
	97 Bk	$5f^9 6d^0 7s^2$	F^8
	98 Cf	$5f^{10} 6d^0 7s^2$	F^9

99 Es	Einsteinium	$5f^{11} 6d^0 7s^2$	f^{10}
100 Fm	fermium	$5f^{12} 6d^0 7s^2$	f^{11}
101 Md	Mendlee	$5f^{13} 6d^0 7s^2$	f^{12}
102 No		$5f^{14} 6d^0 7s^2$	f^{13}
103 Lw		$5f^{14} 6d^0 7s^2$	f^{14}

Three Planet B- uranium, Naphunium, plutonium gone to America came back from california c̄ Einstein Fermi. Mandleer who made Noble Laws.

Oxidation states.

Ac	+2, +3
Th	+2, +3, +4, ~~+5~~
Pa	+3 → +5
U	+3 → +6
Np	+3 → +6
Pu	+3 → +6
Am	+3, +4
Cm	+3 +4
Bk	+3
Cf	+3
Es	+3
Fm	+3
Md	+3
No	—
Lw	—

U, Np, Pu → +6

⇒ All are radioactive in nature.

⇒ +6 O.S. exist in Florwides c̄ U, Np, ~~Am~~, Pu.

+6 ⇒ and also c̄ dioxo cations.

MO_2^{+2}

$\boxed{x = +2+4 = +6}$

UO_2^{+2}

⇒ MO_2^{+} is linear & stable.

⇒ oxocation shows disproportionation rxn in solⁿ as well as solid state.

e.g. $2UO_2^{+} + 4H^{+} \longrightarrow U^{+4} + 2H_2O + UO_2^{2+}$

⇒ **Actinide contraction** It is more dominant than Lanthenide contraction due to more diffused stru. of 5f orbital compared to 4f so that shielding is less. and hence Z_{eff} ↑es, size ↓es.

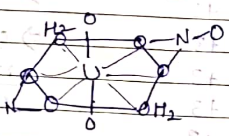
⇒ **Complex formation.**

Because of more actinide contraction.
∵ of high charge density and more diffused shape of f-orbital formed more stable complexes than Ln.
5f participates in bonding, 4f does not.
Higher oxidation state due to involvement of 5f in bonding.

[Actinide forms complexes c̄ π-Ligands]
⇓
due to backbonding.

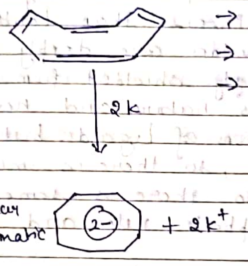
① $Mg(Th(NO_3)_6^{-})$ NO_3^- — bidendate.
C.N. — 12.
$\boxed{x = +4}$ Icosahedral.

② $(UO_2(NO_3)_2 \cdot 2H_2O)$ C.N. — 8
Uranyl nitrate dihydrate.
x − 4 − 2 = 0
$\boxed{x = +6}$



Bicapped Octahedron.

c̄ cyclooctatetraene

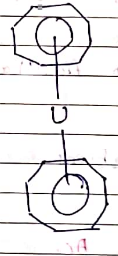


→ tub shaped
→ non-planar
→ non-aromatic

→ Planar
→ Aromatic

This dianion reacts c̄ Ac +4 ions.
U^{+4}, Np^{+4}, Th^{+4}

e.g. $UCl_4 + C_8H_8^{2-}$



→ neutral metallocenes formed.

⇒ **Rxns**

$$UO_2 \xrightarrow{HF} UF_4, \quad UF_6 \xrightarrow{\Delta} UF_4 \; \Big\} \xrightarrow{\Delta} UF_3$$

$$UF_4 \xrightarrow{F} UF_5$$

$$UF_5 \xrightarrow{HF} [UF_6]^-$$

$$[UF_6]^- \xrightarrow[\text{excess}]{HF} [UF_8]^-$$

Spectral properties.

Absorption band of Actinides are 10 times more intense than Lanthenides. The f-orbitals in Lanthenides are deeply burried thus they are largly shielded from environmental factors such as nature and no. of Ligands and vibrations of Ligands. but 5f involved in bonding, so there is mixing of f and d-orbitals so there is some relaxation to Lapporte rule and intense spectra observed.

Colour of Ac. ⇒ mostly coloured to f-f transitions more coloured than the Lanthenides as transitions are not pure f-f. There is mixing of f and d

⇒ ① Ln less basic than Ac. (larger size).

$\boxed{Ln < Ac}$

(ii) Ln do not form oxocations.