

1 H																	2 He						
3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg																	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og						
		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							

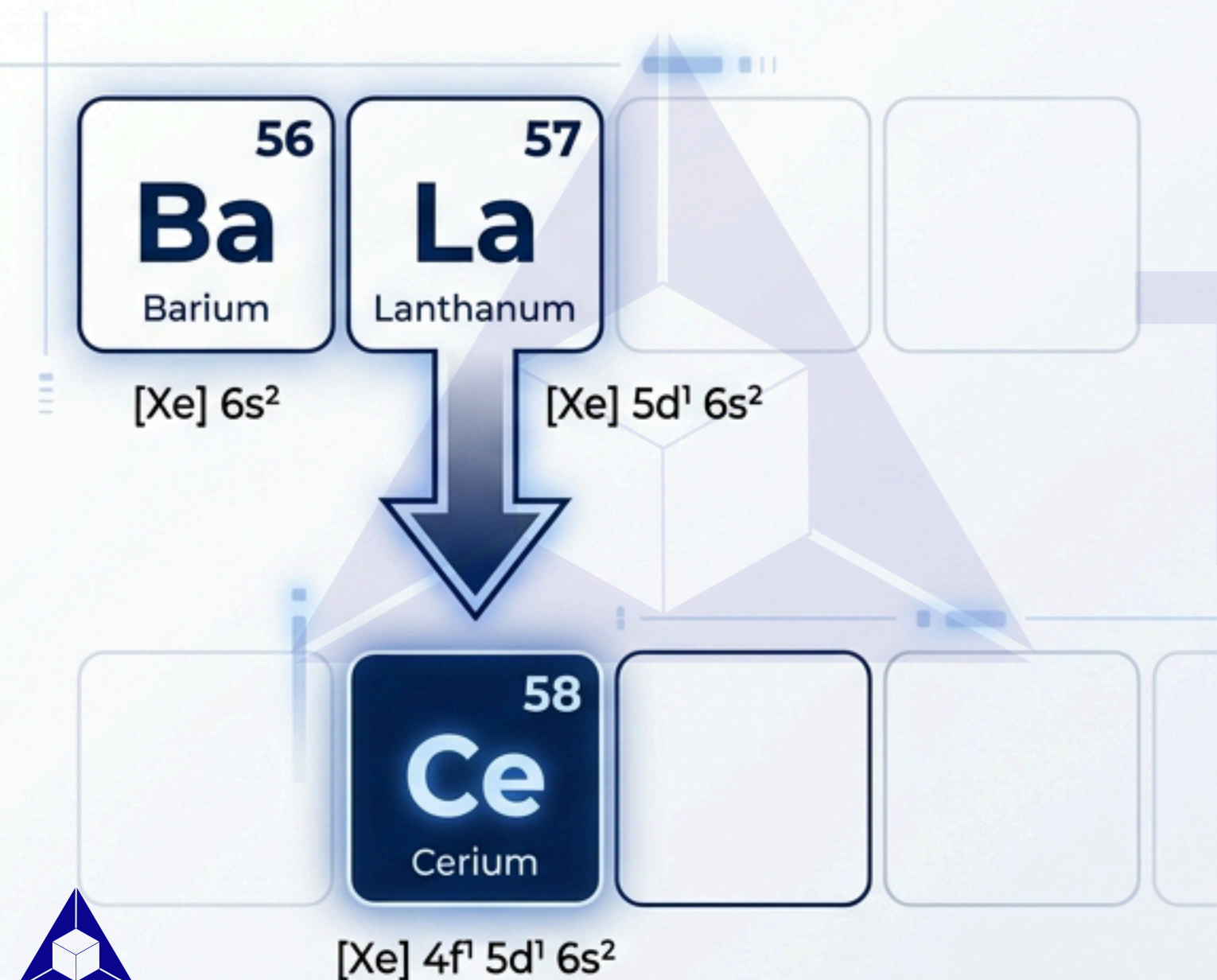
Chapter 4.5

The Lanthanoids

Inner Transition Metals, 4f Series, and the Lanthanoid Contraction.

The Inner Transition Metals

Position: Period 6, Group 3



Consists of 14 elements following Lanthanum (Ce 58 to Lu 71).



Defined by the progressive filling of the **4f orbitals**.



General chemical symbol used in reactions: **Ln**.



Lanthanum (La) is heavily studied alongside them due to extreme chemical resemblance, despite being a **d-block** element.

The Electronic Blueprint

The General Rule

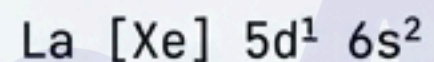


Why 5d sometimes? There is very little energy difference between 4f and 5d orbitals.

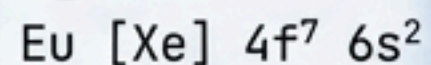
The Exceptions

The Extra Stability Drive

Empty
(f^0):

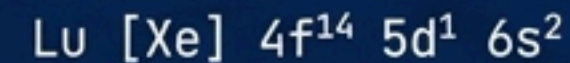
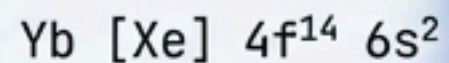


Half-filled
(f^7):



($5d^1$ prevents disrupting stable $4f^7$)

Fully-filled
(f^{14}):

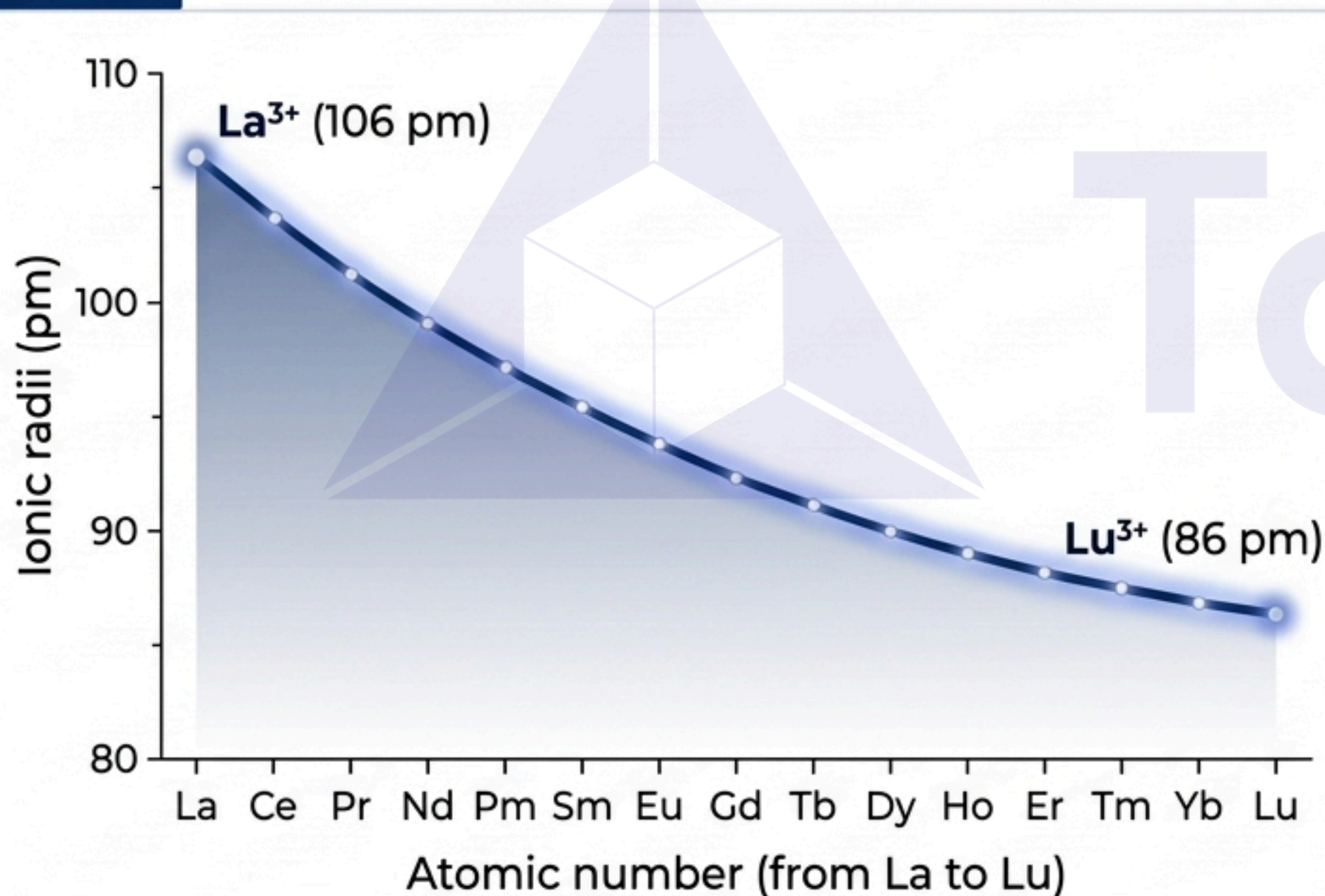


($5d^1$ prevents disrupting stable $4f^{14}$)

The Lanthanoid Contraction

The steady, progressive **decrease** in atomic and ionic radii from Lanthanum to Lutetium.

Data



Mechanism

Electrons enter inner **4f** orbitals.

4f electrons have highly diffused shapes → **Imperfect Shielding**

Nuclear charge (**Z**) increases, but shielding does not compensate.

Effective nuclear charge (**Z_{eff}**) pulls the valence shell inward.

Consequences in the Periodic Table

Impact: The radii of the 3rd transition series (5d) are unexpectedly similar to the corresponding members of the 2nd series (4d).

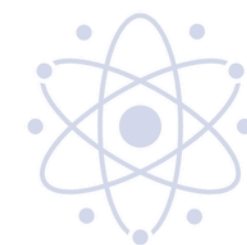


Result: Due to virtually identical sizes and properties, they occur together in nature and are exceptionally difficult to separate.



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$$E=mc^2$$



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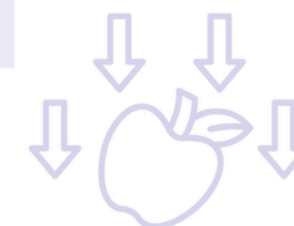
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Key Highlights

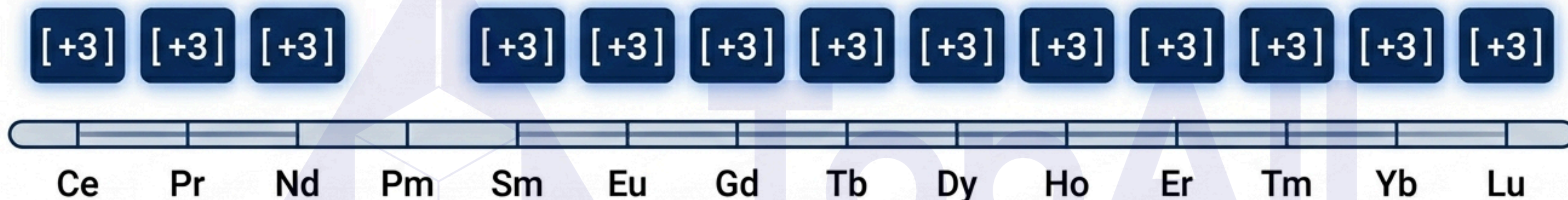
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The Dominance of the +3 State



Ln^{3+} is the most stable and predominant oxidation state across the entire lanthanoid series.



Thermodynamic Driver: Ionisation enthalpies.

Step 1: Abnormally low values for the **3rd ionisation enthalpy** (IE_3) in La, Gd, and Lu provide an extra energy drive.

Step 2: Why? Because losing 3 electrons in these elements perfectly results in highly stable f^0 , f^{10} , f^7 , and f^{14} configurations.

Oxidation Anomalies & Redox Behavior

Deviations (+2 and +4) only occur to achieve f^0 , f^7 , or f^{14} . They act as oxidants/reductants to revert back to the stable +3 state.

Strong Oxidants

Gain e^- to reach +3

1. **$\text{Ce}^{4+} (f^0) \rightarrow$ Reverts to Ce^{3+} .**
 $E^\circ = +1.74\text{V}$. Excellent analytical reagent (reaction is slow).
2. **$\text{Tb}^{4+} (f^7) \rightarrow$ Reverts to Tb^{3+} .**

Strong Reductants

Lose e^- to reach +3

1. **$\text{Eu}^{2+} (f^7) \rightarrow$ Reverts to Eu^{3+} .**
2. **$\text{Yb}^{2+} (f^{14}) \rightarrow$ Reverts to Yb^{3+} .**

Bulk Properties of Ln^{3+} Ions



Colour

Trivalent ions are often coloured in solid state and aqueous solutions.

Cause: f-f transitions (excitation of electrons within the f-level).

Exceptions (Colourless):

$[\text{f}^0]$ (La^{3+} , Ce^{4+})

$[\text{f}^{14}]$ (Lu^{3+} , Yb^{2+})



Magnetism

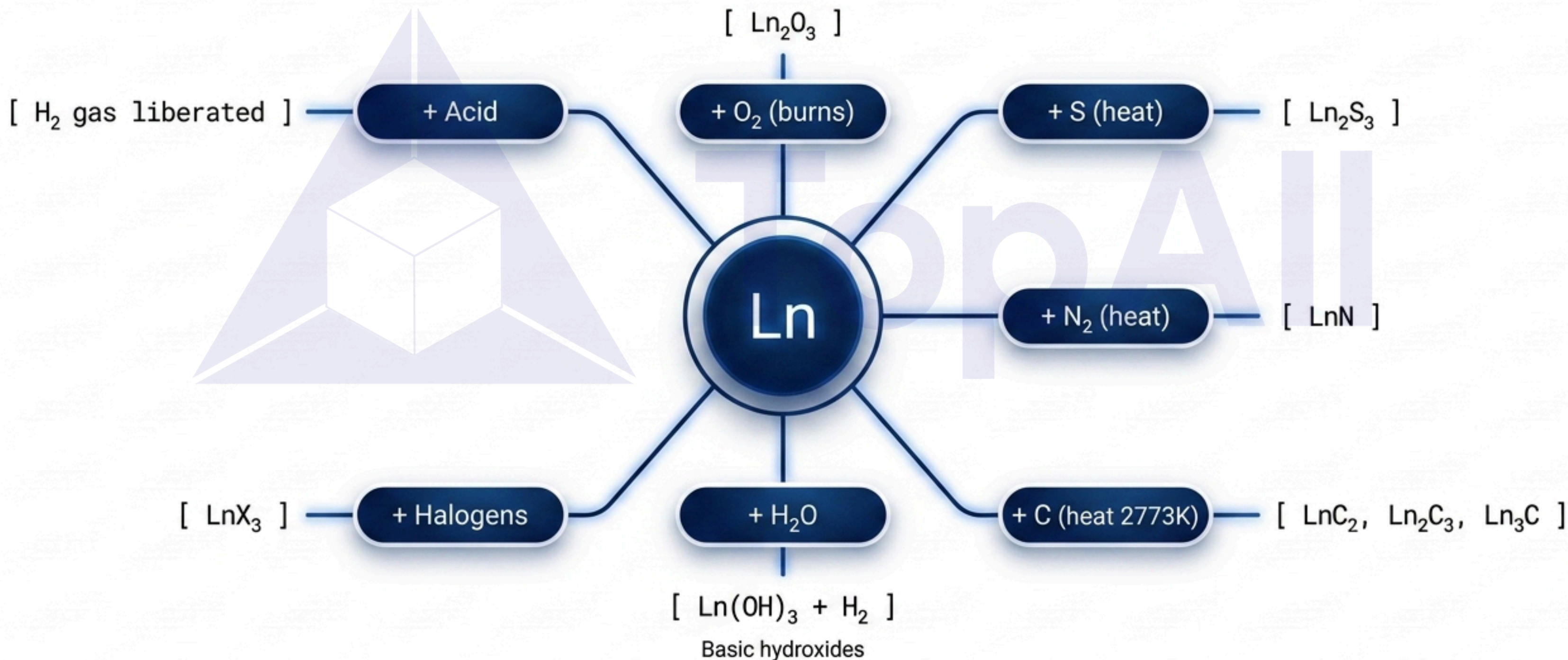
All lanthanoid ions are paramagnetic (due to unpaired f-electrons).

Exceptions (Diamagnetic):

Elements with $[\text{f}^0]$ and $[\text{f}^{14}]$ configurations.

General Chemical Reactivity

Early members react vigorously like Calcium; later members behave more like Aluminium.



Industrial & Commercial Uses



Mischmetal

- Alloy **composition**: ~95% Lanthanoid metal + ~5% Iron + traces of S, C, Ca, and Al.
- **Application**: Used in Mg-based alloys to produce bullets, shells, and lighter flints.



Catalysts

Mixed lanthanoid oxides are essential in petroleum cracking.



Phosphors

Individual Ln oxides emit specific light spectra. Used in television screens and fluorescing surfaces.

High-Yield Exam Summary

⚠️ Top 3 Exam Traps

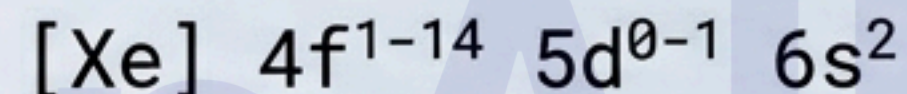
⚠️ **The Zr/Hf Trap:** Zirconium (160pm) and Hafnium (159pm) have identical radii due to the Lanthanoid Contraction.

⚠️ **The Redox Trap:** Ce^{4+} is a strong Oxidant. Eu^{2+} and Yb^{2+} are strong Reductants. All revert to +3.

⚠️ **The Colour/Magnetism Trap:** Look for the configuration. If it is exactly f^0 or f^{14} , it is instantly colourless and diamagnetic.

✅ Core Rules to Memorize

✓ **The Formula:**



✓ **The Anchor:** +3 is the universal stable state for the entire series.



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