▶ Video explanation (YouTube Short)

Lanthanoid Contraction

Zirconium was discovered in the mineral zircon in 1789. Hafnium sat in the very same mineral, yet it was found only in 1923, when Coster and Hevesy picked out its X-ray lines in Copenhagen (Latin *Hafnia*). Chemically, hafnium hid behind zirconium for 134 years. The reason is the **lanthanoid contraction** (NCERT 4.3 and 4.5).

1. The puzzle: Zr and Hf are the same size

Element	Z	Period / shells	Metallic radius
Ti	22	4	147 pm
Zr	40	5	160 pm
Hf	72	6	159 pm

- Going down a group, size normally increases because a new shell is added (Ti → Zr: 147 → 160 pm).
- Hf has 32 more electrons and one more shell than Zr, yet its radius is almost the same (159 pm).

2. What is the lanthanoid contraction?

Lanthanoid contraction: the steady decrease in the size of atoms and ions (Ln^{3+}) from lanthanum to lutetium.

- Between La (Z = 57) and Hf (Z = 72) sit the 14 lanthanoids, Ce (58) to Lu (71).
- Ln^{3+} radius falls steadily: La^{3+} ≈ 103 pm → Lu^{3+} ≈ 86 pm (six-coordinate values). The atomic radii also decrease, but less regularly.

3. Why it happens

- From one lanthanoid to the next, nuclear charge increases by +1 and the new electron enters the **4f** subshell.
- 4f electrons shield the outer electrons **poorly** (shielding: s > p > d > f), because of the diffuse shape of f orbitals.
- So the effective nuclear charge felt by the outer electrons rises at each step and the outer shells are pulled in a little.
- 14 small decreases add up to a large one.

4. Consequences

1. **4d and 5d elements of the same group have almost the same radii:** the contraction across the lanthanoids cancels the increase expected from the extra shell. Zr 160 / Hf 159 pm; Nb and Ta (146 pm); Mo and W (139 pm).
2. **Zr and Hf occur together and are very difficult to separate.** Their chemistry is almost identical. This matters in practice: Zr alloys are used for nuclear fuel tubes because Zr hardly absorbs neutrons, but

Hf absorbs thermal neutrons hundreds of times (≈ 600×) more strongly, so reactor-grade Zr must be almost free of Hf (about 100 ppm or less).

3. **Lanthanoids are difficult to separate from each other**: adjacent members differ only slightly in size.
4. **Basicity of $Ln(OH)_3$ decreases from $La(OH)_3$ to $Lu(OH)_3$**: the smaller Ln^{3+} ion holds OH^- more strongly (more covalent Ln–OH bond), so it releases OH^- less easily.

5. Common mistakes

- ✗ "Hf is bigger than Zr because it has one more shell." ✓ The lanthanoid contraction cancels that increase: Hf ≈ Zr.
- ✗ "4f electrons shield very well because they are inner electrons." ✓ f electrons shield the poorest of all.
- ✗ "Basicity increases from $La(OH)_3$ to $Lu(OH)_3$." ✓ It decreases, as the ion gets smaller.

6. Key takeaways

- Poor shielding by 4f electrons → steady decrease in size from La to Lu.
- It cancels the expected size increase in period 6, so Zr ≈ Hf, Nb ≈ Ta, Mo ≈ W.
- Results: Zr and Hf hard to separate, lanthanoids hard to separate, basicity of $Ln(OH)_3$ decreases La → Lu.

Practice questions

1. (MCQ) Which pair has almost identical atomic radii? (a) Ti, Zr (b) Zr, Hf (c) Sc, Y (d) Cr, Mo
2. (MCQ) The lanthanoid contraction is due to: (a) poor shielding by 4f electrons (b) good shielding by 4f electrons (c) decrease in nuclear charge (d) addition of a new shell
3. (MCQ) The most basic hydroxide is: (a) $Lu(OH)_3$ (b) $Gd(OH)_3$ (c) $La(OH)_3$ (d) $Yb(OH)_3$
4. (MCQ) The order of shielding is: (a) f > d > p > s (b) s > p > d > f (c) d > f > s > p (d) p > s > d > f
5. (Very short) Define lanthanoid contraction.
6. (Very short) Name the 5d element that has nearly the same radius as Nb.
7. (Short) Explain why the atomic radius of Hf is almost the same as that of Zr.
8. (Short) Why are Zr and Hf difficult to separate?
9. (Short) Why does the basicity of lanthanoid hydroxides decrease from $La(OH)_3$ to $Lu(OH)_3$?
10. (HOTS) Y^{3+} has nearly the same radius as Ho^{3+}. With which elements is yttrium found in nature, and why is it hard to separate from them?

Answer key

1. (b) Zr, Hf.
2. (a).
3. (c) $La(OH)_3$.
4. (b).
5. The steady decrease in size of atoms and Ln^{3+} ions from La to Lu.
6. Ta.
7. The 14 lanthanoids come between Zr's period and Hf; poor 4f shielding makes their size shrink steadily, which cancels the increase expected from the extra shell.
8. Their radii (and hence chemistry) are almost identical, a consequence of the lanthanoid contraction.
9. Ln^{3+} gets smaller, so it holds OH^- more strongly (the bond becomes more covalent); OH^- is released less easily.

10. With the heavy lanthanoids (Ho, Dy, Er…) in the same minerals; equal ionic size gives nearly identical chemistry.

▶ Watch the video explanation