▶ Video explanation (YouTube Short)

# The Lanthanoids: Electronic Configuration and Oxidation States

In 1787 a black mineral found at a quarry in Ytterby, Sweden, turned out to contain several new elements (four are named after the village: yttrium, ytterbium, terbium and erbium). They were so alike that it took chemists more than a century to tell all of them apart. These notes explain why the lanthanoids are so similar and why they almost always show +3 (NCERT 4.5).

## 1. Who are the lanthanoids?

- Lanthanum (La, Z = 57) and the fourteen elements that follow it, cerium (Ce, 58) to lutetium (Lu, 71). (Strictly, "lanthanoids" are Ce–Lu; La is included in the discussion because it is so similar.)
- They are placed in a **separate row** at the bottom of the periodic table (with La's position in group 3), otherwise the table would be 32 columns wide.

## 2. Electronic configuration

**General configuration:** $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^{2}$

- Across the series each new electron enters the **4f** subshell, which lies deep inside the atom and is shielded by the filled $5s^2 5p^6$ subshells.
- The outer configuration ($6s^2$) is the same for all, so their chemical properties are very similar.

| Element | Configuration | $Ln^{3+}$ |
|---|---|---|
| La (57) | [Xe] $5d^1\ 6s^2$ | $4f^0$ |
| Ce (58) | [Xe] $4f^1\ 5d^1\ 6s^2$ | $4f^1$ |
| Pr (59) | [Xe] $4f^3\ 6s^2$ | $4f^2$ |
| Eu (63) | [Xe] $4f^7\ 6s^2$ | $4f^6$ |
| Gd (64) | [Xe] $4f^7\ 5d^1\ 6s^2$ (half-filled 4f kept) | $4f^7$ |
| Yb (70) | [Xe] $4f^{14}\ 6s^2$ | $4f^{13}$ |
| Lu (71) | [Xe] $4f^{14}\ 5d^1\ 6s^2$ | $4f^{14}$ |

## 3. Oxidation states

- **+3 is the characteristic oxidation state** of all lanthanoids: the atom loses its two 6s electrons and one more (the 5d electron if present, otherwise one 4f electron). $La^{3+}$ is $4f^0$ and $Lu^{3+}$ is $4f^{14}$.
- Why +3: the energy needed to remove three electrons is more than repaid by the hydration energy (in water) or lattice energy (in solids) of the small, highly charged $Ln^{3+}$ ion.
- **+2 and +4** appear occasionally, mostly when the result is an empty, half-filled or completely filled 4f subshell:

| Ion | 4f | Behaviour |
|---|---|---|
| $Ce^{4+}$ | $4f^0$ (empty) | strong oxidant, reverts to $Ce^{3+}$ ($E°(Ce^{4+}/Ce^{3+}) \approx +1.74$ V) |
| $Tb^{4+}$ | $4f^7$ (half-filled) | oxidant |
| $Eu^{2+}$ | $4f^7$ (half-filled) | strong reducing agent, changes to $Eu^{3+}$ |
| $Yb^{2+}$ | $4f^{14}$ (full) | reducing agent |

Pr, Nd, Tb and Dy also show +4 in oxides of type $MO_2$; Sm shows +2 ($Sm^{2+}$, $4f^6$) although it is not a special configuration, so stability is not the only factor.

## 4. Worked examples

### Example 1

**Q.** Write the configuration of $Ce^{3+}$ and $Ce^{4+}$. **A.** Ce: $[Xe]4f^15d^16s^2$. $Ce^{3+}$: $[Xe]4f^1$. $Ce^{4+}$: $[Xe]4f^0$.

### Example 2

**Q.** Why is $Eu^{2+}$ a strong reducing agent? **A.** It readily loses an electron to reach the common +3 state ($Eu^{3+}$, $4f^6$).

### Example 3

**Q.** Why is $Ce^{4+}$ used as an oxidising agent in analysis? **A.** $Ce^{4+}$ ($4f^0$) strongly tends to gain an electron and return to $Ce^{3+}$ ($E° \approx +1.74$ V).

### Example 4

**Q.** Why are the lanthanoids hard to separate? **A.** The added electrons go into the inner 4f subshell; their outer configuration and ionic sizes are very similar, so their chemistry is almost the same.

## 5. Common mistakes

- ✗ "Lanthanoids show many oxidation states like the d-block." ✓ +3 dominates; +2/+4 only in special cases.
- ✗ "Each new electron goes to the outermost shell." ✓ It goes into the inner 4f subshell.
- ✗ "$Ce^{4+}$ is the most stable state of cerium." ✓ It is a strong oxidant because it tends to return to +3.

## 6. Key takeaways

- $[Xe]4f^{1\text{-}14}5d^{0\text{-}1}6s^2$; electrons fill the deep 4f, so the elements are very similar.
- +3 is the common oxidation state ($La^{3+}$ $4f^0$ … $Lu^{3+}$ $4f^{14}$).
- +4 ($Ce^{4+}$, $Tb^{4+}$) and +2 ($Eu^{2+}$, $Yb^{2+}$) occur near $f^0$, $f^7$, $f^{14}$, but these ions tend to revert to +3.

## Practice questions

1. (MCQ) The general configuration of lanthanoids is: (a) $[Xe]4f^{1\text{-}14}5d^{0\text{-}1}6s^2$ (b) $[Rn]5f^{1\text{-}14}6d^{0\text{-}1}7s^2$ (c) $[Ar]3d^{1\text{-}10}4s^2$ (d) $[Xe]5d^{1\text{-}10}6s^2$
2. (MCQ) The most common oxidation state of lanthanoids is: (a) +2 (b) +3 (c) +4 (d) +5
3. (MCQ) Which is a strong oxidising agent? (a) $Eu^{2+}$ (b) $Yb^{2+}$ (c) $Ce^{4+}$ (d) $La^{3+}$
4. (MCQ) The 4f configuration of $Eu^{2+}$ is: (a) $4f^6$ (b) $4f^7$ (c) $4f^8$ (d) $4f^0$

5. (Very short) Write the electronic configuration of Gd.
6. (Very short) Name a lanthanoid ion with a $4f^{14}$ configuration in the +2 state.
7. (Short) Why is +3 the most common oxidation state of lanthanoids?
8. (Short) Explain why $Ce^{4+}$ is a good oxidising agent and $Eu^{2+}$ a good reducing agent.
9. (Short) Why are the chemical properties of lanthanoids so similar?
10. (HOTS) $Gd^{3+}$ and $Eu^{2+}$: how many 4f electrons does each have? Which electronic feature do they share?

## Answer key

1. (a).
2. (b) +3.
3. (c) $Ce^{4+}$.
4. (b) $4f^{7}$.
5. [Xe] $4f^{7}$ $5d^{1}$ $6s^{2}$.
6. $Yb^{2+}$.
7. Removing $6s^{2}$ and one more electron costs energy that is more than repaid by the hydration / lattice energy of $Ln^{3+}$; this holds for all members.
8. $Ce^{4+}$ ($4f^{0}$) gains an electron easily to become $Ce^{3+}$; $Eu^{2+}$ ($4f^{7}$) loses one easily to become $Eu^{3+}$: both revert to the common +3 state.
9. Electrons are added to the inner 4f subshell, shielded by $5s^{2}5p^{6}$; the outer $6s^{2}$ configuration and ionic sizes are similar.
10. Both are $4f^{7}$ (half-filled 4f subshell).

▶ Watch the video explanation