LANTHANOIDS & ACTINOIDS (Inner transition metals)

Lanthanoids — (Ln) → generic symbol

General formula for f-block elements

$(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

- $n=6$ → Lanthanoids: $4f^{1-14}5d^{0-1}6s^2$
- $n=7$ → Actinoids: $5f^{1-14}6d^{0-1}7s^2$

↳ La ⟶ Lu (15 elements) (known as ~~actinoids~~ Lanthanoids), characterized by gradual filling of the 4f subshell.

↳ the relative energies of nd & (n-1)f are similar.

↳ Stable f^7 configuration found in Eu, Gd, Am & Cm.

↳ 4f-orbital is buried.

↳ Generally resemble each other in their chemical & physical properties.

Oxidation states —

↳ Characteristic oxidation state = +3

↳ Almost similar in size, so difficulties arise in separation.

↳ More similar to alkali or alkaline earth metals.

↳ $Ln + H_2O \longrightarrow H_2\uparrow$

↳ known as rare earth metal.

↳ Not resemble to transition metals.

—i) First three ionization energies are smaller as compared to transition metals like Chromium or Cobalt.

—ii) Ln have low heat of atomization than transition metals.

↳ Eu & Yb ⟶ +2 O.S. (very stable)

↓ ↓

$4f^7$ $4f^{14}$

(half filled) (completely filled)

— similar to alkaline earth metals (Be, Mg, ...

(have lowest enthalpies of vaporization, largest atomic radii ⟶ similar to Ba

— $Eu \xrightarrow{Liq.\ NH_3} Eu^{2+} + (2e^-)$ ⟶ conducts electricity

solvated

⟶ blue soln.

↳ Aq. soln of Eu^{2+}, Yb^{2+} & Sm^{2+} can be prepared.

In aq. soln ⟶

- oxidized by oxygen
- reduce water.

↳ Nd, Dy, Tm, Ho ⟶ stable as solids as M(II).

↳ LaI_2, CeI_2 etc. ⟶ Formulated as $M^{3+}(I^-)_2e^-$

↳ contain delocalized e^-s. ⟶ metallic lustre, electrical conductivity

↳ Higher than +3 O.S. exhibited by Ce, Pr & Tb.

Ce^{4+} —

- Ce^{4+} is stable (kinetically in water)
- very strong oxidizing agent in H_2O ($E^0 = 1.74\,V$) (eg:- Cerium(IV) ammonium nitrate)
- Used as a volumetric standard in redox titrations.

Lanthanide Contractions —

As a consequence of the poor shielding of the 4f electrons, there is a steady increase in effective nuclear charge and concomitant reduction in size with increasing atomic number in the series from left to right.

F- orbitals —

↳ Ungerade
↳ Asymmetrical with respect to inversion.

↳ Split by an octahedral field into three levels —

t_{1g}, t_{2g}, & a_{2g}.

Differences between the 4f & 5f Orbitals –

4f	5f
1) Dont have radial node	1) Have a radial node
2) Buried so deeply within the atom	2) In earlier elements of actinide series are available for bonding.

→ they are differs in the radial part but not in the angular part.

Absorption Spectra of Lanthanide –

↳ Result due to f-f transition

↳ Absorption spectras are sharp & line like-
— Broadening effect of ligand vibrations is minimized because the 4f-orbitals in the lanthanides are buried deep within the atom.

↳ f-f transition analogous to d-d transition but ~~d-d~~ not broad like absorptions of transition metals.

Magnetic Properties of the Lanthanides —

↳ Spin - orbit coupling is large & only ground state is populated.

↳ Paramagnetic moment of the lanthanide ions —

$$\mu = g[J(J+1)]^{1/2}$$

where, J = total angular momentum quantum no.

g = Landé splitting factor for the e⁻.

— Originates from spin & orbital motions of the unpaired e⁻s.

↳ Ligand-field effects are small.

↳ For Sm^{3+} & Eu^{3+} — spin-orbit coupling is not large enough.

Actinides—

↳ Ac ⟶ Lr

↳ Properties are similar to Lanthanides.

↳ 5f – orbital

↳ $5f^{1-14}6d^{0-1}7s^2$

↳ Radioactive, glow in dark, toxic.

Oxidation states —

↳ Thorium & Uranium ⟶ +4 O.S.

↳ Shows higher O.S., since 5f – orbitals are available for bonding.

↳ Up to +7 oxidation state.

↳ Higher oxidation states are represented by stable actinyl ions eg:- MO_2^+, MO_2^{2+} etc.

Actinide Contractions —

— Steady decrease in size in the series from left to right.

Absorption Spectra of Actinides—

— 5f – orbitals in the lighter actinide elements results in a greater Ligand – metal orbital interaction due to greater

exposure of 5-f-orbitals.

↳ Absorption spectra somewhat broad.

↳ With increasing nuclear charge, 5f-orbitals behave like 4f-orbitals in the Lanthanides & spectra of the heavier actinides become more Lanthanide-like.

Magnetic Properties –

↳ Quite complex.

↳ Paramagnetic moment vary with temp^{r}.

↳ lower than those of the corresponding Lanthanides.

↳ Spin-orbit coupling and ligand field effects are of comparable magnitude.

Comparison of Inner Transition & Transition Metals —

Lanthanide	First transition metals
1) 4f-orbital	1) 3-d orbital
2) Common co-ordination no.s — 6, 7, 8, 9	2) Common co-ordination no.s — 4, 6
3) Weak metal-ligand orbital interaction	3) Strong metal-ligand orbital interaction

4) Soln complexes are ionic, & rapid ligand exchange takes place	4) Soln complexes are co-valent, co-valent complexes exchange ligand slowly.
5) Ionic radii — 106 – 85pm	5) Ionic radii — 75 – 60 pm
6) Bond strength determined by electronegativity of the ligand eg:- $F^- > OH^- > H_2O > NO_3^- > Cl^-$	6) Bond strength determined by orbital interaction — eg:- $CN^- > NH_3 > H_2O > OH^- > F^-$

↳ Lanthanides typically behave like hard acid. Preferencially attracted towards hard ligands eg:- fluoride & oxygen donor ligands.

↳ Minimizes Ligand field stabilization energies (LFSE).

— So reduces overall stability of the complex.

— Provides a greater flexibility in geometry & co-ordination no.

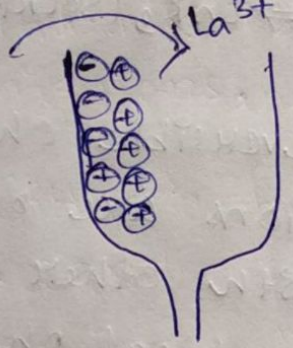
↳ Complexes are labile in soln.

↳ The early (or largest) elements of series generally shows higher C.N.

Lanthanide separation —

↳ Ion-exchange chromatography.

La^{3+} separation —



→ Cation exchange column

→ ~~Reagents~~ — resin — { sulphonated polystyrene

Lanthanides are placed on ion-exchange resin & eluted with a complexing agent.

SO_3H, $-COOH$ gps

La^{3+} (resin)

↳ La (left) → Lu (right)

$Ln^{3+}(aq) + HR \longrightarrow LnR_3$ solid $+ 3H^+(aq)$

size decreases

(large size) (small size)

$LaX_3.nH_2O$ $LuX_3.nH_2O$

(n = small) (n = large)

order of elution —

Lu → La

Ion-exchange Method — In this method synthetic cation resins are used. These resins contain $-SO_3H$ / $-COOH$ groups and the hydrogen in these resins is replaced with lanthanide ions. The aqueo-

- Its solution contains a mixture of Ln^{3+}, which is allowed to pass down a column with cation exchange resin.

$$Ln^{3+}(aq) + 3HR(solid) \rightleftharpoons LnR_3(solid) + 3H^+(aq)$$

(Ion exchange is a reversible chemical reaction where dissolved ions are removed from solution replace with other ions of the similar or same electrical charge)

The Lanthanides ions are stick to the resin with various strengths based on their size. The lanthanum ion, being smallest binds most tightly to the resin, where the largest ion Lutetium binds the weakest. Then the Lanthanides are washed out of the ion exchange column with various eluant agent or complexing agent such as citrate ion or α-hydroxyisobutyrate ion and emerging one at a time & so are separated. During this process ions of the eluating agent replace Ln^{3+} ion that is fixed on the resin & Ln^{3+} reacts with the complex ion (eg:- citrate ion to form the Ln-citrate complex) & form complex.

Miscellaneous —

↳ Fifteen elements from La → Lu are lanthanoids (according to IUPAC). Whereas fourteen elements Ce → Lu without lanthanum are lanthanides (meaning the elements similar to lanthanum)

↳ Major sources of ~~the~~ lanthanides are Monazite sand composed of phosphate of thorium, cerium, neodymium & lanthanum The phosphate portion of monazite contains small traces of other lanthanide ions.

↳ Promethium doesnot occure naturally.

↳ Lanthanide & Actinide ions are weakly coloured.

↳ f-e^s are practically unaffected by complex formation, hence colour remains almost constant for a particular ion regardless of the ligands.

↳ Absorption bands due to f-f transition are sharp compared to the broad bands for d-d transition.

↳ Absorption bands due to 4f—5d transitions are broad & are affected by

ligand environment.

↳ All lanthanoide ions [except La^{3+} (f^0) & Lu^{3+}(f^{14})] show luminescence.
— Eu^{3+} (f^6) & Tb^{3+} (f^8) show particularly strong emissions.

↳ Lanthanoide complexes used as phosphors on TV screens & fluorescent lighting due to their luminiscence property.

↳ Ce show f-d transition in UV-region
Yb show f-f " " IR-region

Lanthanides	Actinides
i) 4f	i) 5f
ii) Zero radial node	ii) One radial node
~~iii) Z_{eff} is highly sensitive~~	iii) diffused or less core like
iii) Inner orbital	iv) earlier Actinides & latere Actinides are studied differently
iv) Z_{eff} is highly sensitive to energy of 4f-orbital Large gap between 4f & 5d	Latere Actinides are resemble to lantha-nides.