F-Block Elements

The Inner Transition Elements

* Partly filled f. subshells (ie n-2th energy shells)
* Elements are also called inner transition Elements.

(1) Lanthanide Series
(2) Actinide Series.

The Lanthanide Series:

* Lanthanum (La) 57 to next fourteen elements 57 to 71.

Lanthanides are also known as Lanthanones.

* Electronic configuration of these 14 Elements resembles to Lanthanides so their qualities resemble to each other.
* Configuration of Lanthanum is $[Xe]5d^1 6s^2$.
* In succeeding 14 elements electrons are filled in 4f subshell.

Electronic configuration of cerium starts with $[Xe]4f^1 5d^1 6s^2$ and ends up to Lutium as $[Xe]4f^{14} 5d^1 6s^2$.

* La and Lu have similar chemical and Physical properties.

Occurance:

* Lanthanides are originally called Rare Earth elements.
* Earth is used because occured in form of oxides.
* Rare was used because their occurance was believed to be very searce.

* Most commonly occuring Lanthanide is Cerium.
* Monazite is most important mineral containing Lanthanides.
* Monazite is Lanthanide orthophosphate.
* Monazite also contains Thorium.
* Elements having even atomic number are relatively more abundant, and have larger number of isotopes.
* Elements having odd atomic number are less abundant.
* Element Promethium (Z=61 Pm) does not exist is nature.
* (Pm) Promathium is a man made element.
* Promathium is formed by artificial radioactive disintigration.

Properties of Lanthanides:

Electronic Configuration:

Element Symbol	Name of Element	Electronic configuration	Electronic Structure/ Configuration of M^{3+} ion.	Oxidation states.
Prototype La	Lanthanum	$[Xe]\ 5d^1\ 6s^2$	$[Xe]$	+ III
Ce	Cerium	$[Xe]\ 4f^1\ 5d^1\ 6s^2$	$[Xe]\ 4f^1$	+ III (+ IV)
Pr	Praseodymium	$[Xe]\ 4f^3\ 5d^0\ 6s^2$	$[Xe]\ 4f^2$	+ III (+ IV)
Nd	Neodymium	$[Xe]\ 4f^4\ 5d^0\ 6s^2$	$[Xe]\ 4f^3$	(+ II) + III
Pm	Promethium	$[Xe]\ 4f^5\ 5d^0\ 6s^2$	$[Xe]\ 4f^4$	(+ II) + III
Sm	Samarium	$[Xe]\ 4f^6\ 5d^0\ 6s^2$	$[Xe]\ 4f^5$	(+ II) + III
Eu	Europium	$[Xe]\ 4f^7\ 5d^0\ 6s^2$	$[Xe]\ 4f^6$	+ II + III
Gd	Gadolinium	$[Xe]\ 4f^7\ 5d^1\ 6s^2$	$[Xe]\ 4f^7$	+ III
Tb	Terbium	$[Xe]\ 4f^9\ 5d^0\ 6s^2$	$[Xe]\ 4f^8$	+ III (+ IV)
Dy	Dysprosium	$[Xe]\ 4f^{10}\ 5d^0\ 6s^2$	$[Xe]\ 4f^9$	+ III (+ IV)
Ho	Holmium	$[Xe]\ 4f^{11}\ 5d^0\ 6s^2$	$[Xe]\ 4f^{10}$	+ III
Er	Erbium	$[Xe]\ 4f^{12}\ 5d^0\ 6s^2$	$[Xe]\ 4f^{11}$	+ III
Tm	Thulium	$[Xe]\ 4f^{13}\ 5d^0\ 6s^2$	$[Xe]\ 4f^{12}$	(+ II) + III
Yb	Ytterbium	$[Xe]\ 4f^{14}\ 5d^0\ 6s^2$	$[Xe]\ 4f^{13}$	(+ II) + III
Lu	Lutetium.	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$	$[Xe]\ 4f^{14}$	+ III

Oxidation States.

* In Lanthanides +III oxidation state is common.
* In Lanthanids the oxidation states given in ( ) are either doubtful or very unstable
* In Lanthanids the oxidation states other than above may exist. but less important
* Oxidation states {+II} and {+IV} occur when an element leads to formation of.

1. A noble Gas configuration
   eg. Ce^{4+} (f^0)
2. A Half filled f shell
   eg. Eu^{2+}, and Tb^{4+} (f^7)
3. A completly filled f level.
   eg. Yb^{2+} (f^{14})

* The only (+IV) and +II states which have any aquous chemistry are Ce^{4+}, Sm^{2+}, Eu^{2+} and Yb^{2+}.

* Ionic Radii

Ions	La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}	Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}
Radius (A°)	1.15, 1.11, 1.09, 1.08, 1.06, 1.04, , 1.02, 1.00, 0.99	0.97, 0.96, 0.95, 0.94, 0.93

* Ionic Size decreases as we move along the lanthanide series from Lanthanum to Lutetium.
* As we see on moving from La^{3+} to Lu^{3+} the ionic radius shrinks from 1.15 to 0.93A°
* This steady decrease in ionic radius all along the series upto 0.22A° is called the Lanthanide contraction.
* Lanthanide contraction is an important factor for saparation of Lanthanides from one another
* Lanthanide contraction have significant effect on the relative properties of the elements. which precede and follow the Lanthanide in periodic table.
* Radius of La^{3+} = 1.15 A°
  Radius of Y^{3+} = 0.93 A°
  ] difference .224°

Sc 1.44	Ti 1.32	V 1.22
Y 1.62	Zr 1.45	Nb 1.34
La 1.69	Hf 1.44	Ta 1.34

58 to 71

14 Lanthanides

* Radius of ~~Hf~~ Hf^{4+} = .814°] diff. .014°
  Zr^{4+} = .80 A

Causes of Lanthanide Contraction:

* Addition of f electrons increases the attraction force and Radius contracts
* Shielding effect of f electrons are less than that of even d electrons.
  this causes reduction of size of 4f ⁿ. subshell which results in Lanthanide contraction.

Complex Formation:

* Lanthanids have +3 charge which is quite high but due to thir larger size their charge density is low.
* So they have less polarig power
* So they have very less tendency to form complex ion.

* Complexes with unidentate ligands are very few
* Complexes with a few chelating ligands are found. commonly (chelating ligands. β-diketones, oximes, EDTA).
* Lanthanids do not form complexes with π bonding ligands lik CO, NO, CNR.
* Tendency to form complexes increase with increase in atomic Number.

Monazite Sand

containing a Mixture of phosphates of Lanthanides, thorium, Zirconium etc.

Digest with Conc. H_2SO_4 at 200°C

Paste Form.
containing sulphates of Lanthanides, etc + Phosphoric acid.

Treat with cold water

- Residue: Silica and Zircon.
- Solution: Sulphates of Lanthanides and thorium + Phosphoric acid.

Dilute and Adjested pH in alkaline range

- Residue: Phosphate of thorium.
- Solution: Sulphates of Lanthanides

Add. Na_2SO_4

- Residue: Double Sulphates of light Lanthanides (La to Sm)
- Solution: Simple Sulphates of heavy lanthanids (Gd to Lu)

Ammonium Cerium (IV) sulphate : (CAS)

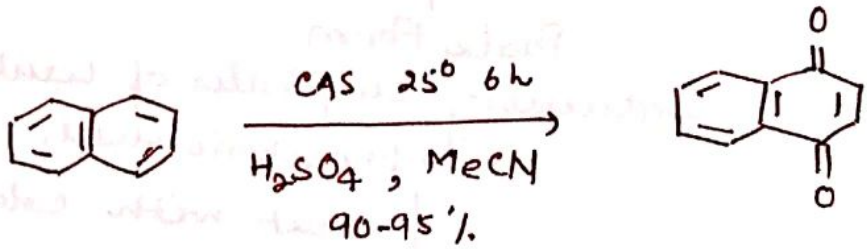
Colour:- Orange-Red
- Water soluble

Formula. $(NH_4)_4 Ce(SO_4)_4 \cdot 2H_2O$

Use in analytical chemistry :

- Analytical reagent in T.L.C. (thin layer chromatography for detection of antidepressant drug in human blood and urine sample.

- Reagent for oxidation of aromatic rings, halophenols, for regioselective, Bayer-Villiger oxidation and oxidative aromatization



CAN - Ceric Ammonium Nitrate → Works same as CAS. but efficiency is moderate but in case of CAS yield is greater than that of CAN

Chemistry of Actinides

* From Actinium ($_{89}Ac$) to Lawrencium ($_{103}Lr$)
* Electron (14) successively filled in to antepenultimate 5f subshell.
* Also known as Second Inner Transition series.
* All the actinids resemble to each other very closly.

Electronic Configuration:

Oxidation States

* All Actinides have an oxidation state of +3 like lanthanides.
* But +3 is not the most stable oxidation state always.
  (+3) It is not most stable for Th, Pa, U, Np.
* +3 is stable oxidation state for the elements $_{95}Am \rightarrow {}_{103}Lw$ except $_{102}No$.
* Most stable oxidation for first four elements are Th (+IV), Pa (+V) and U (+VI)
* Most stable oxidizing state for Np is (+V)
* Pu shows the ox. state from +III to +VII
  But most stable state for Pu is +IV
* M^{+4} ions are known in acid solution, and are precipitated by F^-, PO_4^{3-} and IO_3^- ions.
* the Elements all form solid dioxides MO_2 ✓ and fluorides MF_4. ✓
* +V state is most stable for Pa and Np. very few solid compounds are know..
* M^{5+} ions do not occur in solution, but MO_2^+ ion exist between pH 2-4. and these oxaions are linear in structure
  $[O-M-O]^+$
* +VI states exists as Fluorids MF_6 for elements U, Np, Pu and Am.
* more widely found as dioxoion MO_2^{2+}
  It is also linear
  $[O-M-O]^{2+}$

Symbol	Name of Element	Electronic Configuration	Oxidation States
Ac	Actinium	$[Rn]\ 6d^1\ 7s^2$	(+2) +3 (+4)
Th	Thorium	$[Rn]\ 6d^2,\ 7s^2$ ✓✓	(+3), +4, (+5)
Pa	Protactinium	$[Rn]\ 5f^2, 6d^1\ 7s^2$	(+3) +4, +5, +6
U	Uranium.	$[Rn]\ 5f^3\ 6d^1\ 7s^2$	+3, +4, +5, +6
Np	Neptunium	$[Rn]\ 5f^4\ 6d^1\ 7s^2$	+3, +4, +5, +6
Pu	Plutonium	$[Rn]\ 5f^6\ 6d^0\ 7s^2$	+3, +4, +5, +6
Am	Americium	$[Rn]\ 5f^7\ 6d^0\ 7s^2$	+3, (+4)
Cm.	Curium	$[Rn]\ 5f^7\ 6d^1\ 7s^2$	+3, (+4)
Bk	Berkeylium	$[Rn]\ 5f^9\ 6d^0\ 7s^2$	+3, +4
Cf	Calformium	$[Rn]\ 5f^{10}\ 6d^0\ 7s^2$	+3
Es	Einsteinium	$[Rn]\ 5f^{11}\ 6d^0\ 7s^2$	+3
Fm	Fermium	$[Rn]\ 5f^{12}\ 6d^0\ 7s^2$	+3
Md	Mendelevium	$[Rn]\ 5f^{13}\ 6d^0\ 7s^2$	+3
No	Nobelium	$[Rn]\ 5f^{14}\ 6d^0\ 7s^2$	—
Lr	Lawrencium	$[Rn]\ 5f^{14}\ 6d^1\ 7s^2$	—

* Lower ox. states tend to be ionic. higher ox. states are covalent.
* M^{2+}, M^{3+}, M^{4+} ions are known.
* Hydrolysis of these ions ~~are~~ occurs quite readily, but can be suppressed by using acid solutions.
* Perchloric acid is most suitable acid for this as it has a little tendency to form complexes.
* Hydrolysis of higher oxidation states give (+V) $\longrightarrow$ MO_2^+ ions and (+VI) $\longrightarrow$ MO_2^{2+} ions

Separation of Neptunium (Np), Plutonium (Pu) and Americium (Am) from Uranium

Neptunium (Np) Plutonium (Pu) Americium (Am) are produced from uranium in nuclear reactors.

$$^{235}_{92}U + {}_0n^1 \longrightarrow {}_{92}U^{236} + {}_0n^1 \longrightarrow {}_{92}U^{237} \xrightarrow{-(-1\beta^0)} {}_{93}Np^{237}$$

$$^{238}_{92}U + {}_0n^1 \longrightarrow {}_{92}U^{239} \xrightarrow{-(-1\beta^0)} {}_{93}Np^{239} \xrightarrow{-(-1\beta^0)} {}_{94}Pu^{239}$$

$$^{239}_{94}Pu \xrightarrow{({}_0n^1, \gamma)} {}_{94}Pu^{240} \xrightarrow{{}_0n^1, \gamma} {}_{94}Pu^{241} \xrightarrow{-(-1\beta^0)} {}_{95}Am^{241}$$

$$^{238}_{92}U \xrightarrow{+{}_0n^1} {}_{92}U^{239} \xrightarrow{-2({}_0n^1)} {}_{92}U^{237} \xrightarrow{-(-1\beta^0)} {}_{93}Pu^{237}$$

Separation of Np, Pu and Am from U is based on following chemistry:

1. Stability of Oxidation states

$$Am^{3+} > Pu^{3+} >> Np^{3+}, U^{4+}$$

in case of oxo ions

$$UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+}$$

2. Extraction in to organic solvents:

* MO_2^{2+} ions form solutions and they can be extracted in to organic solvents.
* M^{4+} ions are extracted in to tributyl phosphate in kerosene from 6M HNO_3 solution.
* M^{3+} ions are extracted from 10-16 M HNO_3.

3. Precipitation Reactions - Actinides in +3 and +4 oxidation states can be precipitated as their ~~fluo~~ fluorides and phosphates from acid solutions.

* ~~+4 oxi~~ Beyond (+4) oxidation states either does not precipitate or prevented from precipitation by complex formation with sulphate ions.