

2. Chemistry of The f-Block Elements

- There are two series of inner transition elements
- The first series, from cerium to lutetium, is called the **lanthanides**
- They are characterized by the filling up of the 4 f energy levels which are not usually involved in bonding
- The second series of elements, from thorium to lawrencium, is called the **actinides**.

- f-block elements

- ➔ Lanthanides(also called lanthanoids) are called first inner transition series

- ➔ Lanthanides and actinides known as inner transition elements

- ➔ Lanthanides commonly called the **rare earths**.

➤ The word 'earth' was used because they occur as oxides, which in early usage meant earth, and the word rare was used because of the **great difficulty in their separation from each other**. Otherwise, these are not particularly rare in earth's crust.

		GROUPS																	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	1	1 H																	2 He
	2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
	3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	4	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
	5	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
	6	55 Cs	56 Ba	57 La	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
	7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub						
6th-period subset					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	
7th-period subset					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	

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Electronic Configurations

- ❖ La has one **5d** and two **6s** electrons;
- ✓ the next element **cerium**, however, while still retaining two **6s** electrons has two electrons in the **4f** orbital and none in the **5d** orbital.
- The atoms of the elements from **cerium** to **lutetium** have between 2 and 14 electrons in the 4f orbital.

- ❖ This configuration for **La** is an exception: it is expected to be $[\text{Xe}^{54}]6s^2 4f^1$ but experimental data (spectral lines) indicate that its correct assignment is the $[\text{Xe}^{54}]6s^2 5d^1$. **La, Z= 57,**
 $[\text{Xe}^{54}] 5d^1 6s^2$
- ✓ The valence shell electronic configuration of these elements can be represented as $(n - 2)f^{0-14}(n - 1)d^{0-1}ns^2$.

Ce, Z= 58, $[\text{Xe}^{54}] 4f^1 5d^1 6s^2$

Pr, Z= 59, $[\text{Xe}^{54}] 4f^3 6s^2$

Nd, Z= 60, $[\text{Xe}^{54}] 4f^4 6s^2$

Eu, Z= 63, $[\text{Xe}^{54}] 4f^7 6s^2$

Dy, Z= 66, $[\text{Xe}^{54}] 4f^{10} 6s^2$

Yb, Z= 70, $[\text{Xe}^{54}] 4f^{14} 6s^2$

Lu, Z= 71, $[\text{Xe}^{54}] 4f^{14} 5d^1 6s^2$

Electronic Configuration

Element name	Symbol	Z	Ln	Ln ³⁺	Radius Ln ³⁺ / pm
Lanthanum	La	57	[Xe]6s ² 5d ¹	[Xe]4f ⁰	116
Cerium	Ce	58	[Xe]4f ¹ 6s ² 5d ¹	[Xe]4f ¹	114
Praesodymium	Pr	59	[Xe]4f ³ 6s ²	[Xe]4f ²	113
Neodymium	Nd	60	[Xe]4f ⁴ 6s ²	[Xe]4f ³	111
Promethium	Pm	61	[Xe]4f ⁵ 6s ²	[Xe]4f ⁴	109
Samarium	Sm	62	[Xe]4f ⁶ 6s ²	[Xe]4f ⁵	108
Europium	Eu	63	[Xe]4f ⁷ 6s ²	[Xe]4f ⁶	107
Gadolinium	Gd	64	[Xe]4f ⁷ 6s ² 5d ¹	[Xe]4f ⁷	105
Terbium	Tb	65	[Xe] 4f ⁹ 6s ²	[Xe]4f ⁸	104
Dysprosium	Dy	66	[Xe] 4f ¹⁰ 6s ²	[Xe]4f ⁹	103
Holmium	Ho	67	[Xe] 4f ¹¹ 6s ²	[Xe]4f ¹⁰	102
Erbium	Er	68	[Xe] 4f ¹² 6s ²	[Xe]4f ¹¹	100
Thulium	Tm	69	[Xe] 4f ¹³ 6s ²	[Xe]4f ¹²	99
Ytterbium	Yb	70	[Xe] 4f ¹⁴ 6s ²	[Xe]4f ¹³	99
Lutetium	Lu	71	[Xe] 4f ¹⁴ 6s ² 5d ¹	[Xe]4f ¹⁴	98

Rare Earth Metals



Lanthanide
series

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
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Actinide
series

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
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f-block elements are called
inner-transition elements

2.1. General Physical and Chemical Properties

Physical Properties

Melting and Boiling points

- Lanthanides have fairly high melting points.
However, no definite trend is observed in melting and boiling points from La to Lu.

Atomic and ionic size

- The atomic and ionic sizes decrease steadily in going from Ce to Lu.
- ✓ In the atoms of lanthanides, the nuclear charge increases with atomic number, and the added electrons go to the inner 4f orbitals. The shielding effect of 4f electrons from the increased nuclear charge is poor. Thus, as the atomic number increases, the effective nuclear charge experienced by each 4f electron increases. This causes

- The successive contractions accumulate and the total effect for all the lanthanides is called **lanthanide contraction**.

Consequences of Lanthanide Contraction

The lanthanide contraction has a highly significant effect on the relative properties of the elements which precede and follow lanthanides in the periodic table.

- i. **Basicity of ions:** Due to lanthanide contraction, the size of Ln^{3+} ions decreases regularly with increase in atomic number.
- ✓ According to **Fajan's rule**, decrease in size of Ln^{3+} ions increase the covalent character and decreases the basic character between Ln^{3+} and OH^- ion in $\text{Ln}(\text{OH})_3$.
- ✓ Since the ionic radii of Ln^{3+} ions decrease in moving from left to right in the series. Thus, **$\text{La}(\text{OH})_3$ is the most basic**, while **$\text{Lu}(\text{OH})_3$ is the least**.

- ii. Regular decrease in their tendency to act as **reducing agent**, with increase in atomic number.
- iii. Due to lanthanide contraction, **second and third rows of d-block transition elements are quite close in properties**
- iv. Due to lanthanide contraction, **these elements occur together in natural minerals and are difficult to separate.**
- v. Due to the lanthanide contraction, **the atomic size of the post-lanthanide elements** (elements following the last element of the lanthanide series) becomes small.

Density

- Lanthanides have high densities ranging between 6.77 to 9.74 gcm⁻³.
- ✓ The densities, in general, increase with increase in atomic number.

Magnetic properties

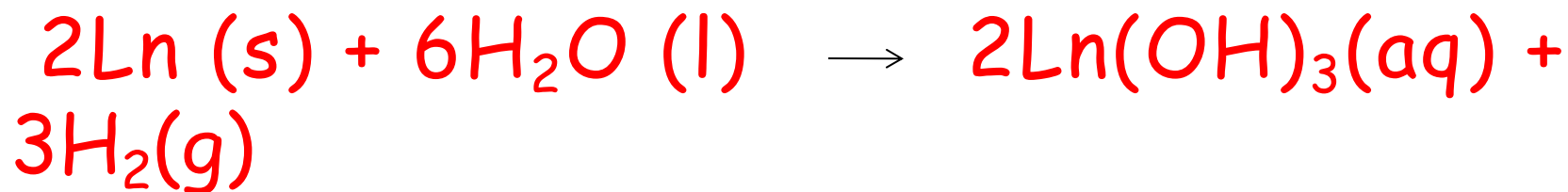
- La^{3+} and Lu^{3+} are diamagnetic, while the trivalent ions of the rest of the lanthanides are paramagnetic in nature.
- ✓ In other word, all lanthanide ions with the exception of Lu^{3+} , Yb^{2+} and Ce^{4+} are paramagnetic because they contain unpaired electrons in the 4f orbitals.

Chemical Properties

In chemical reactivity, they resemble calcium.

- readily tarnish in air and burn to give oxides (all give trioxides except Ce which forms CeO_2).
- combine with the non-metals -N, S, halogens, H.

- The hydrides are non-stoichiometric but have a composition of MH_3
- . These hydrides liberate hydrogen from water.
- The lanthanides also liberate hydrogen from water.



- Lanthanide compounds are generally predominantly ionic and usually contain lanthanide metal in its +3 oxidation states.

Oxidation States

- exhibits a principal oxidation state of +3
 - The +3 ions of La, Gd and Lu which contain
 - empty
 - half-filled
 - completely filled 4f level
- } are especially stable.
- Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with La^{+3} i.e. an empty 4f level-noble gas configuration)

- Tb^{+4} exists which has the same electronic structure as Gd^{+3} i.e. a half-filled 4f level.
- An empty, a half filled and a completely filled 4f shell confers some extra stability

$\text{La}^{+3} 4f^0 5s^2 5p^6$ (empty 4f level)

$\text{Ce}^{+4} 4f^0 5s^2 5p^6$ (empty 4f level)

$\text{Gd}^{+3} 4f^7 5s^2 5p^6$ (half-filled 4f level)

$\text{Tb}^{+4} 4f^7 5s^2 5p^6$ (half-filled 4f level)

❖ Eu^{+2} is isoelectronic with Gd^{+3}

i.e. half-filled 4f level

Yb^{+2} is isoelectronic with Lu^{+3}

Gd^{+3} $4f^7 5s^2 5p^6$

Eu^{+2} $4f^7 5s^2 5p^6$ (half-filled 4f level)

Lu^{+3} $4f^{14} 5s^2 5p^6$

Yb^{+2} $4f^{14} 5s^2 5p^6$ (completely filled 4f)

➤ +2 and +4 states exist for elements that are close to these states.

e.g. Sm^{+2} and Tm^{+2} occur with f^6 and f^{13} arrangements

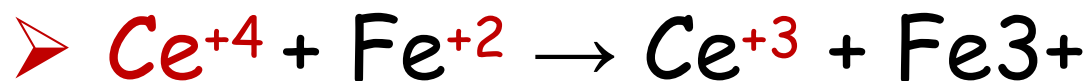
✓ Pr^{+4} and Nd^{+4} have f^1 and f^2 arrangements.

➤ The most stable oxidation state is Ln^{+3} and

✓ Ln^{+2} and Ln^{+4} are less stable.

✓ Ce^{+4} is strongly oxidizing and

✓ Sm^{+2} is strongly reducing:



➤ { Ce^{+4} and Sm^{+2} are converted to +3 state,

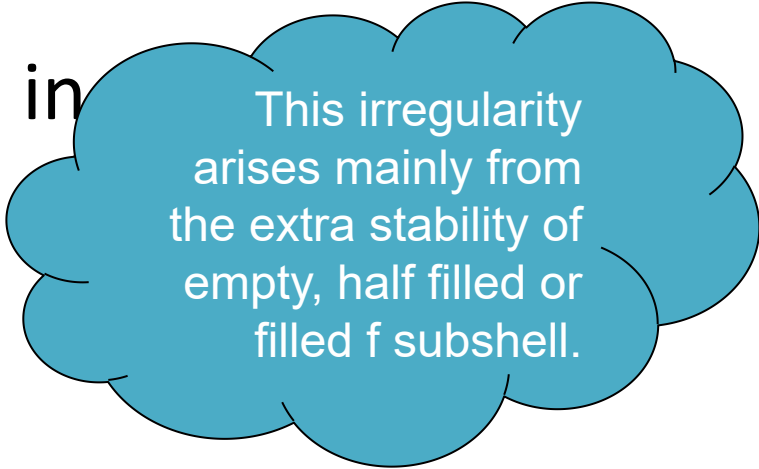
➤ showing that it is the most stable oxidation state}

CHEMICAL PROPERTIES OF THE COMPOUNDS OF VARIOUS OXIDATION STATES

Oxidation State(+3)

- The trivalent state is characteristics of all the lanthanides.

Occasionally +2 and +4 ions in solution or in solid compounds are also obtained.

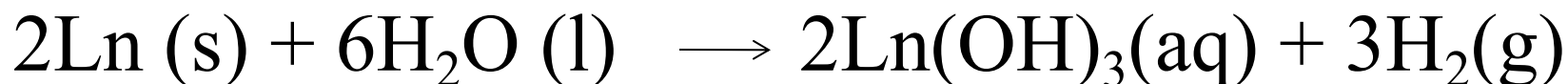


This irregularity arises mainly from the extra stability of empty, half filled or filled f subshell.

□ They are more reactive than **aluminum** and slightly more than **magnesium**

Hydroxides

❖ React slowly with cold water, but more rapidly on heating to form the hydroxide.



➤ The hydroxides are ionic and basic

✓ less basic than Ca(OH)_2

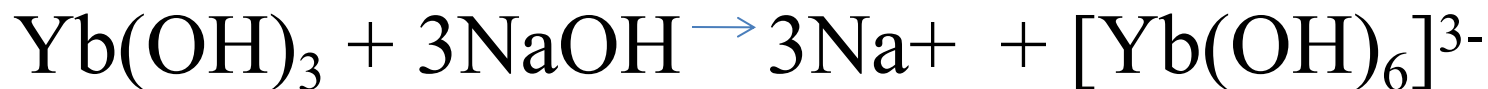
✓ more basic than Al(OH)_3 which is **amphoteric**.

❑ The basicities of the hydroxides decreases with increasing atomic number.

✓ $\text{Ce}(\text{OH})_3$ is the most basic

✓ $\text{Lu}(\text{OH})_3$ is the least basic.

➤ The decrease in basic properties can be seen by dissolving the hydroxides in hot concentrated sodium hydroxide which produces complexes.



Oxides

- ❖ Lanthanides readily tarnish in air and on heating in oxygen, give the oxides, Ln_2O_3
- Cerium alone forms CeO_2 .
- Yb and Lu form a protective oxide film which prevents the whole metal forming oxide unless heated to 1000°C .

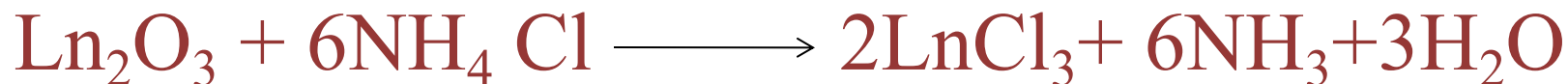
Hydrides

- ❖ Formed when the metal reacts with H_2 . Requires heating up to $300-400^\circ\text{C}$ to initiate the reaction.
- ✓ **Eu and Yb** which form the divalent compounds **EuH_2 and YbH_2** .
- ✓ The hydrides generally, liberate hydrogen from water, are stable to heat up to 900°C and react with O_2 to form the oxide.



Halides

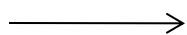
- LnX_3 can be prepared by heating the metal and the halogen.
- It can also be prepared by heating the oxide with an excess of ammonium halide.



❖ If the hydrated halides are heated, they form **oxohalides** .

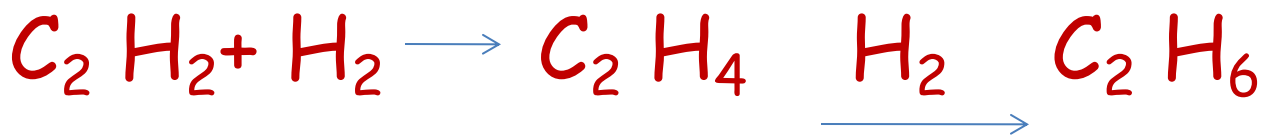
✓ However cerium gives **CeO₂**

The bromides and iodides are similar to chlorides.



Carbides

- The lanthanides also form **carbides**
- ✓ They are formed by the arc melting of the metals with carbon in an inert atmosphere
- ✓ LnC_2 are more reactive than CaC_2 .
- ✓ They react with water to give ethyne, hydrogen, ethane and ethene



Oxidation State(+2)

➤ Sm, Eu and Yb have aqueous chemistry at oxidation state(+II).

[Sm⁺² Eu⁺² and Yb⁺²].

The most stable is Eu⁺² which is stable in water but the solution is strongly reducing.

Extraction and Separation of the Lanthanides

- Major sources of lanthanides are **Monazite sand**-composed of phosphates of **thorium**, **cerium**, **neodymium** and **lanthanum**
 - **Bastnaesite** , is a mixed fluorocarbonate $M^{III}CO_3F$ where M is La or the lanthanide metals.
- They are extracted from the earlier mentioned **ores**

- Monazite is treated with hot concentrated H_2SO_4
- ✓ Th, La and the Ln dissolve as sulphates and are separated from insoluble material.
- Th is precipitated as ThO_2 by partial neutralization with NH_4OH .
- ✓ Na_2SO_4 is used to salt out La and the lighter Ln as sulphates, leaving the heavy lanthanides in solution.

- The light Ln are oxidized with bleaching powder $\text{Ca}(\text{OCl})_2$
- Ce^{2+} is oxidized to Ce^{4+} which is precipitated as $\text{Ce}(\text{IO}_3)_4$ and removed.
- ✓ The extraction process from **bastnaesite** is slightly simpler since it does not contain **Th**.

separation

Reduction of their Trihalides

➤ La, Ce, Pr, Nd and Gd may be obtained by reduction of their trichlorides with calcium at about 1000°C in an argon filled vessel



✓ The heavier Ln like Tb, Dy, Ho, Er and Tm can also be obtained by this method but the trifluorides is used, since their trichloride is volatile.

- Also since the heavier Ln have higher melting points and so require a temperature of 1400°C.
- ✓ At this temperature CaCl_2 boils.
- ✓ Li is sometimes used instead of Ca.



Eu, Sm and Yb are obtained by chemical reduction of their trioxides.

Ion exchange

- ❖ The based on their ability to form **complex ions**
- All lanthanides form +3 ions, M^{+3} whose ionic radii decrease progressively with increasing atomic number from Ce^{+3} to Lu^{+3} .
- As a solution containing +3 lanthanides ions is placed at the top of a column of **cation exchange resin**

- [e.g. is **Dowex-50** made of a sulphonated polystyrene and contains functional groups **–SO₃H.**]
- The Ln^{+3} ions are absorbed into the resin and an equivalent amount of hydrogen ions are released from the column



Cation exchanger

- A citrate buffer (citric acid/ammonium citrate) solution is slowly run down the column and the cations partition themselves between the column itself and the moving citrate solution.
- ✓ smaller ions show a greater preference for complexing with the citrate solution, these ions are the first to emerge from the column.

By the correct choice of conditions

- the lutetium ion, $\text{Lu}^{3+} (\text{aq})$, emerges first from the column, followed by the cations;
- ✓ ytterbium, thulium, erbium, etc, in order of increasing ionic radius.

Valency change

- The different properties of the various oxidation states makes separation very easy
i.e the properties of Ln^{+4} and Ln^{+2} are very different from that of Ln^{+3} .
- Cerium can be separated from Ln mixtures because it is the only one which has a Ln^{+4} ions stable in aqueous solution.
- ✓ A solution containing mixture of Ln^{+3} ions can be oxidized with NaOCl under alkaline conditions to produce Ce^{+4} .

- Because of the higher charge, Ce^{+4} is much smaller and less basic than Ce^{+3} or any other Ln^{+3} .

The Ce^{+4} is separated by carefully controlled precipitation of CeO_2 or $\text{Ce}(\text{IO}_3)_4$, leaving the trivalent ions in solution.

Also, Eu^{+2} can be separated from a mixture of Ln^{+3} .

❖ If a solution of Ln^{+3} ions is reduced electrolytically using a Hg cathode or Zn amalgam,

✓ Eu^{+2} is produced.

✓ If H_2SO_4 is present, EuSO_4 which is insoluble will be precipitate.

This can be filtered off.

Coordination Compounds

- Ln^{+3} forms complexes of high coordination numbers.
- ✓ The coordination numbers for $[\text{Ln}(\text{OH}_2)_n]^{+3}$ in aqueous solution are up to 9
- ✓ The Ln^{+3} ions readily form complexes with F- and O- donor ligands

Eg with H_2O , EDTA, β -diketonate, citric acid, oxalic acid ligands.

Spectra of Lanthanoid complexes

- Lanthanide ions are weakly coloured.
- ✓ The spectra of their complexes show much narrower and more distinct absorption bands which is associated with *weak $f-f$ transition*.
- ✓ *The 4f orbital* are deeply embedded inside the atom and well shielded by 5s and 5p electrons.

- The f electrons are practically unaffected by complex formation
- ✓ hence colour remains almost constant for a particular ion regardless of the ligands
- The bands due to *f-f transition* are sharp compared to the broad bands for *d-d transition*.

Uses

Best single use of the lanthanoids is for the production of alloy steels for plates and pipes.

A well known alloy is misch metal which consists of a lanthanoid metal (~95%) and iron (~5%) and traces of S, C, Ca and Al. A good deal of misch metal is used in Mg based alloy to produce bullets, shell and lighter flint.

Mixed oxides of lanthanoids are employed as catalysts in **petroleum cracking**.

- ❖ Use in the glasses industry
- ❖ Use in the metallurgical industry
- ❖ Use in the television industry
- ✓ small amount of europium oxide (Eu_2O_3) is added to yttrium oxide (Y_2O_3), it gives a brilliant-red phosphor.

Colour television screens utilize red, green, and blue phosphors.

The Actinides(5f- Block elements)

- Result from the filling of the 5f orbitals.
- The elements in which the extra electron enters 5f- orbitals of $(n-2)^{\text{th}}$ main shell are known as 5f-block elements, actinides or actinones.

Actinide Contraction

- ❖ **The shielding of one f-electron by another from the effect of nuclear charge** is quite weak on account of the shape of the f- orbital, hence with increasing atomic number, the effective nuclear charge experienced by each 5f-electron increases. This causes shrinkage in the radius of atoms or ions as one proceed from Ac to Lw. This accumulation of successive shrinkage is called actinide contraction.

All isotopes are radioactive, with only ^{232}Th , ^{235}U , ^{238}U and ^{244}Pu having long half-lives.

Only Th and U occur naturally-both are more abundant in the earth's crust than tin.

The others must be made by nuclear processes.

Some characteristic properties of actinides

The dominant oxidation state of actinides is +3. Actinides also exhibit an oxidation state of +4. Some actinides such as uranium, neptunium and plutonium also exhibit an oxidation state of +6.

The actinides show actinide contraction (like lanthanide contraction) due to poor shielding of the nuclear charge by 5f electrons.

All the actinides are radioactive. Actinides are radioactive in nature. So the study of their chemistry is difficult in the laboratory. Their chemistry is studied using tracer techniques.

Electronic configuration

Element name	Symbol	Z	Ln	Ln ³⁺	Radius Ln ³⁺ / pm
Actinium	Ac	89	[Rn] 6d ¹ 7s ²	[Rn]5f ⁰	111
Thorium	Th	90	[Rn]4f ¹ 5d ¹ 7s ²	[Rn]5f ¹	
Protactinium	Pa	91	[Rn]5f ² 6d ¹ 7s ²	[Rn]5f ²	
Uranium	U	92	[Rn]5f ³ 6d ¹ 7s ²	[Rn]5f ³	103
Neptunium	Np	93	[Rn]5f ⁴ 6d ¹ 7s ²	[Rn]5f ⁴	101
Plutonium	Pu	94	[Rn]5f ⁶ 7s ²	[Rn]5f ⁵	100
Americium	Am	95	[Rn]5f ⁷ 7s ²	[Rn]5f ⁶	99
Curium	Cm	96	[Rn]5f ⁷ 6d ¹ 7s ²	[Rn]5f ⁷	99
Berkelium	Bk	97	[Rn]5f ⁹ 7s ²	[Rn]5f ⁸	98
Californium	Cf	98	[Rn]5f ¹⁰ 7s ²	[Rn]5f ⁹	98
Einsteinium	Es	99	[Rn]5f ¹¹ 7s ²	[Rn]5f ¹⁰	
Fermium	Fm	100	[Rn]5f ¹² 7s ²	[Rn]5f ¹¹	
Mendelevium	Md	101	[Rn]5f ¹³ 7s ²	[Rn]5f ¹²	
Nobelium	No	102	[Rn]5f ¹⁴ 7s ²	[Rn]5f ¹³	
Lawrencium	Lr	103	[Rn]5f ¹⁴ 6d ¹ 7s ²	[Rn]5f ¹⁴	

Comparison of Lanthanides and Actinides

Similarities

Lanthanides and actinides involve filling of f-orbitals and thus are similar in many respects.

The most common oxidation state is +3 for both lanthanides and actinides.

Both are electropositive in nature and thus very reactive.

Magnetic and spectral properties are exhibited by both lanthanides and actinides.

Actinides exhibit actinide contraction just like lanthanides.

Differences

- Besides +3, lanthanides also show oxidation states of +2 and +4 while actinides show higher oxidation states of +4, +5, +6 and +7 as well.

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw
						+2								
+3	-	-	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
	+4	+4	+4	+4	+4	+4	+4	+4						
		+5	+5	+5	+5	+5								
			+6	+6	+6	+6								
				+7	+7									

- Lanthanide ions are colourless while most of the actinide ions are coloured.
- Actinides have a greater tendency towards complex formation as compared to lanthanides.
- Lanthanide compounds are less basic while actinide compounds have appreciable basicity

- Actinides form few important oxocations such as UO_2^{2+} , PuO_2^{2+} , etc, while such oxocations are not known for lanthanides.
- Almost all actinides are radioactive while lanthanides, except promethium, are non-radioactive.
- The magnetic properties of the actinides ions are considerably more difficult to explain than those of the lanthanide ions.