T.Y.B.Sc. Chemistry

Paper –II Inorganic Chemistry

Sem- IV

Chapter -1. Chemistry of f- Block Elements



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HRM Chemistry Notes

Chapter -1 Chemistry of F-Block Elements

Inorganic chemistry covers the chemistry of over 100 elements. Though eachelement has its individual characteristics, there are patterns and trends that provide a framework of order.

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The transition elements may be defined as those elements having partly filled 'd' or 'f' shells in their atoms or ions. There are total 59 transition elements. They are subdivided into two main groups:

- Main transition elements called d-block elements
- Inner transition elements called f-block elements

The elements in which electrons are enter in the (n- 2)f orbital called as **f-block** elements. These elements are also known as Inner Transition Elements, because the f-orbitals are not penultimate butantepenultimate. The two series of elements in the f block derive from the filling of the seven 4f and 5f orbitals, respectively. The valence shell electronic configuration of these elements can be represented as $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$

These elements are further divided as Lanthanide elements and Actinide elements in which 4f and 5f orbitals are filled by 14 electrons. This occupation of f orbitals from f^1 to f^{14} corresponds to the elements cerium (Ce) to lutetium (Lu) in Period 6 called Lanthanide Series and from thorium (Th) to lawrencium (Lr) in Period 7 called Actinide Series.

However, given the similarity of their chemical properties, the elements lanthanum (La) and actinium (Ac) are normally included indiscussion of the f block. The lanthanides are sometimes referred to as the '**rare earth elements**'. That name, however, is inappropriate because they are not particularly rare, except for promethium, which has no stable isotope. A general lanthanides is represented by the symbol **Ln** and an actinides by **An**.

The Lanthanide series

The series of elements in which 4f orbitals are successively filled by electrons are called as Lanthanides. They are also termed as lanthanones or lanthanoids or 4f-blok elements.

- Lanthanum: La⁵⁷:
- Cerium: Ce⁵⁸ :
- Praesodymium: Pr⁵⁹ :
- Neodymium: Nd⁶⁰ : [Xe]4f⁴6s²
- Promethium: Pm⁶¹:
- Samarium: Sm⁶²:
 Europium: Eu⁶³:
- [Xe]4f⁵6s² [Xe]4f⁶6s²

[Xe]6s²5d¹

[Xe]4f16s25d1

 $[Xe]4f^{3}6s^{2}$

- [Xe]4f⁷6s²
- Terbium: Tb⁶⁵ : [Xe] $4f^{9}6s^{2}$ • Dysprosium: Dy⁶⁶ : [Xe] $4f^{10}6s^{2}$ • Holmium: Ho⁶⁷ : [Xe] $4f^{11}6s^{2}$
- Holmium: Ho⁶⁷:
 Erbium: Er⁶⁸:
- Thulium: Tm⁶⁹ :
- Ytterbium: Yb⁷⁰:
- Lutetium:Lu⁷¹ :
- [Xe] 4f¹⁴6s² [Xe]4f¹⁴6s²5d¹

 $[Xe] 4f^{12}6s^2$

[Xe] 4f136s2

• Gadolinium: Eu⁶⁴: **[Xe]4f⁷6s²5d**¹

Position of Lanthanide elements in the periodic table:

The lanthanides are belongs to Group IIIA in the 6^{th} period of periodic table. Their actual position is in between La⁵⁷ to Hf⁷².

- All 14 elements possess the same number of valence electrons and hencethey can form M^{3+} ions. All have similar electronic configuration.
- All these elements have similar chemical and physical properties. Hencethese elements must be placed in the same group
- All 14 lanthanide elements have atomic weights in between those of Ba⁵⁶ and Hf⁷² and hence must be placed in between these two elements. Barium is belongs to II group and Hafnium is IV group of periodic table.

• These elements also resemble Y^{39} and Sc^{21} which are the members off IIIB group of periodic table.

Electronic configuration:

There is some uncertainty about electronic configuration of lanthanides. The general electronic configurations of lanthanides are $4f^{0-14}$, $5d^{0/1}$, $6s^2$.

- Lanthanum has electron configuration: La [Xe]⁵⁴, 4f⁰, 5d¹, 6s². It does not possess any 4f electron. This is definite.
- The next electron after lanthanum does not enter the expected 5d sublevel,but enters the 4f sublevel.

Chemistry of F-block element

- As the atomic number increases by one i.e. Ce⁵⁸ to Lu⁷¹, all 14 electrons areenters in the f-orbital.
- The valence shell electron configuration of the lanthanides can be represented as, 4f¹ to 14, 5d¹, 6s².
- Only La, Gd and Lu possess a single 5d electron. Other lanthanides do nothave electrons in the 5d orbital.
- The filling of 4f orbital is not regular.
- The f^0 , f^7 and f^{14} configurations are most stable because empty, half-filled and completely filled orbitals are stable. Thus La has empty (f^0), Gd has half-filled (f^7) and Lu has completely filled (f^{14}) orbitals.
- There is large difference in the properties of the lanthanides and d-block elements.
- The 4f electrons in the antepenultimate shell are totally protected from surrounding ions by overlying 5s and 5p electrons

At.	Name	Symbol	Ln	Ln ²⁺	Ln ³⁺	Ln ⁴⁺
No						
(Z)		-	577 7 4 20		FTT 7.4 0	
57	Lanthanum	La	$[Xe]4f^{0},$		$[Xe]4f^{0},$	-
			5d ¹ ,6s ²		5d°,6s°	
58	Cerium	Ce	$[Xe]4f^1,$	-	$[Xe]4f^1,$	-
			5d ¹ ,6s ²		5d ⁰ ,6s ⁰	
59	Praseodymium	Pr	$[Xe]4f^3$,	- J -	$[Xe]4f^2$,	-
			$5d^{0}, 6s^{2}$		5d ⁰ ,6s ⁰	
60	Neodymium	Nd	[Xe]4f ⁴ ,	-	$[Xe]4f^3,$	-
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	
61	Promithium	Pm	[Xe]4f ⁵ ,	-	[Xe]4f ⁴ ,	-
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	
62	Samarium	Sm	[Xe]4f ⁶ ,	[Xe]4f ⁶ ,	[Xe]4f ⁵ ,	-
			$5d^{0},6s^{2}$	$5d^{0}, 6s^{0}$	$5d^{0}, 6s^{0}$	
63	Europium	Eu	[Xe]4f ⁷ ,	[Xe]4f ⁷ ,	[Xe]4f ⁶ ,	-
			$5d^{0}, 6s^{2}$	$5d^{0}, 6s^{0}$	$5d^{0}, 6s^{0}$	
64	Gadolinium	Gd	[Xe]4f ⁷ ,	-	[Xe]4f ⁶ ,	-
			$5d^{1},6s^{2}$		$5d^{1},6s^{0}$	
65	Terbium	Tb	[Xe]4f ⁹ ,	-	[Xe]4f ⁸ ,	[Xe]4f ⁷ ,
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	$5d^{0}, 6s^{0}$
66	Dysprosium	Dy	[Xe]4f ¹⁰ ,	-	[Xe]4f ⁹ ,	[Xe]4f ⁸ ,
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	$5d^{0}, 6s^{0}$
67	Holmium	Но	[Xe]4f ¹¹ ,	-	$[Xe]4f^{10}$,	-
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	
68	Erbium	Er	$[Xe]4f^{12}$,	-	$[Xe]4f^{11}$,	-
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	
69	Thulium	Tm	$[Xe]4f^{13}$,	-	$[Xe]4f^{12}$,	-
			$5d^{0}, 6s^{2}$		$5d^{0}, 6s^{0}$	
70	Yetterbium	Yb	[Xe]4f ¹⁴ .	[Xe]4f ¹⁴ ,	$[Xe]4f^{13}$,	-
			$5d^{0}, 6s^{2}$	5d ⁰ ,6s ⁰	$5d^{0}, 6s^{0}$	
71	Lutetium	Lu	[Xe]4f ¹⁴ .	-	[Xe]4f ¹⁴ ,	-
			$5d^{1}, 6s^{2}$		$5d^{0}, 6s^{0}$	

Oxidation states:

The lanthanide elements are highly electropositive. They exhibits in +II, +III and +IV oxidation states. The most common, stable and characteristic oxidation state of lanthanides is +III, while +II and +IV oxidation sates are not common and less stable.

Ln(+III) compounds

- The lanthanides exhibit a principal oxidation state of +3.
- The +3 in La, Gd and Lu are especially stable because +3 ions of these elements have an **empty**, **a half-filled and completely** filled 4f sub-shell respectively.
- The trivalent lanthanides mostly form ionic salts.

Ln(+II) compounds

- The most common divalent derivatives of the lanthanides are for Eu⁺², which achieves a favourable f⁷ configuration (half filled).
- The simple salts include YbI2, EuI2, and SmI2. NdI2, DyI2 and TmI2. Samarium iodide (SmI2) is a useful reducing agent.

Ln(+IV) compounds

- Tetravalent lanthanides are rare. Ce⁺⁴ in **ceric ammonium nitrate** is a useful oxidising agent.
- Ce and Tb also exhibit oxidation state of +4. Although a few lanthanidesexhibit oxidation states of +4 and +2.
- The common Ce^{+4} compounds are CeO₂, CeF₄, Ce(SO₄)₂, Ce(NO₃)₄, etc.

Occurrence of Lanthanides:

Other than promethium (Pm), the lanthanides are reasonably common in the Earth's crust; indeed, even the 'rarest' lanthanides, thulium, has a crustal abundance that is similar to that of iodine. The principal mineral source for the early lanthanides is *monazite sand*, (Ln,Th)PO4, which contains mixtures of lanthanides and thorium. Another phosphate mineral, *xenotime* (of similar composition, LnPO4), is the principal source of the heavier lanthanides.

The common oxidation state for all the lanthanides is Ln(III), which makes separation difficult, although cerium, which can be oxidized to Ce(IV), and europium, which can be reduced to Eu(II), are separable from the other lanthanides by exploiting their redox chemistry. Separation of the remaining Ln^{3+} ions is accomplished on a large scale by multistep liquid-liquid extraction in which the ions are distributed between an aqueous phase and an organic phase containing complexing agents. Ion-exchange chromatography is used to separate the individual lanthanide ions when high purity is required. Pure and mixed lanthanidemetals are prepared by the electrolysis of molten lanthanide halides.

Separation of the Lanthanides:

The lanthanides in their +III oxidation sate are very similar to each other in chemical properties that their separation by chemical methods is very difficult, except for cases where the separation can be brought about by making use of valence difference. Thus lanthanides are separated from each other on the basis of slight difference in their physical properties, such as solubility, hydration, stability, complex formation and adsorption. These physical methods can be broadly classified into the following methods...

2/3 of world production is actually used mixed in the proportions occurring naturally in the ore.

- Cerium & Europium may be extracted chemically: Oxidize only Ce to M⁴⁺ by HClO or KMnO4, then precipitate as CeO2 or Ce(IO3)4, On action of Zn/Hg only Eu forms a stable M²⁺ that doesn't reduce H₂O, then isolate by precipitation as EuSO4
- Separation by Fractionation: Small Scale methods used originally.
- Fractional Crystallization: Ln(NO3)3.2NH4NO3.4H2O or Ln(BrO3)3
- Fractional Thermal Decomposition: Ln(NO3)3
- **Complex formation** with EDTA These methods are now out-dated.

Ion-Exchange Method:

This is most effective general method for the separation and purification of lanthanides. It is the most important and rapid method. It is type of column chromatography. Tha column is packed with cation exchange resin. $Ln^{3+}(aq)$ are strongly adsorbed by a cation-exchange resin add an *eluant* ligand typically *chelating* ligands. *E.g.* EDTA, or 2-OH-EDTA, HIB {[[alpha]]-hydroxyisobutyric acid}

Ligand binds most strongly to smallest ion and gives Ln(EDTA) complexes. Ln3+ions present in aqueous solution that passes through resin.

$$Ln^{3+} + 3H+R^- \Box Ln^{3+}3R^- + 3H^+$$

Then Column washes with water then by buffer solution Ammonium citratepH 4-7



$$Ln^{3+3}R^{-} + 3NH4^{+} = Ln^{3+} + 3NH4R$$

It gives Ln-citrate complex

 Ln^{3+} + citrate ion = Ln-citrate complex

The citrate solution is comes down the column, the lanthanide ions comes out of the resin and forms citrate complex and go back on the resin. This process is repeated many times as the metal ion gradually moves down to the column. The order of displacement of cation is generally inversely proportional to their atomic number. Elution orderis Lu > La, means lutetium comes out first and lanthanum last. By using this method, the elements obtained are about 99.90% pure.

Solvent extraction method:

This method is based on the difference in the distribution coefficient i.e. solubility of the salt of lanthanides between water and immiscible organic solvent. Ln³⁺(aq) is extracted in a continuous counter-current process in **Craig Apparatus** into a non-polar organic liquid tributyl phosphate (TBP), Heavier Ln³⁺ ions are moresoluble in TBP than lighter ions. TBPtributyl phosphate dissolved in kerosene. This process is automatic multistep, counter-current **HRM Chemistry Notes**

conditions gives 99.9% purity Ln metals. Many extractions can be carried out in Craig Apparatus.

Lanthanide Contraction:

The decrease in the atomic and ionic radii of the lanthanide elements with increasing atomic number is called **Lanthanide Contraction**.

The causes of lanthanide contraction:

- All 14 electrons are added in 4f subshell, not in outer shell i.e. sixth orbital.
- As the atomic number increases, each element contains one more electron and one proton in the nucleus i.e. nuclear charge increases.
- The 4f electrons are ineffective in screening the outer electrons from the nucleus causing imperfect shielding. Shielding effect is very poor.
- As a result, there is a gradual increase in the nucleus attraction for the outer electrons. Consequently gradual decrease in size occurs. This is called lanthanide contraction.

Hence with increase in atomic number and nuclear charge, the effective nuclear charge felt by each 4f electron increases. This causes a contraction or shrinkage in the radii of the atom and ions as goes from La to Lu. This successive decrease in size is called lanthanide contraction.

Consequences of Lanthanide contraction:

- All the lanthanides possess very **similar properties**: because due to lanthanide contraction, they are very small deference in ionic radii.
- Separation of these elements is very difficult: because due to lanthanide contraction, ionic radii of Y, Dy, Ho are same, thus properties of these elements are also similar.
- **High density**: due to small atomic size, the metallic crystals become more compact. Thus density is very high. It ranging between 6.7 to 9.74 g.cm⁻³. The densities, in general, increase with increase in atomic number. Highest density 9.84 (Lu); lowest 5.24 (Eu).
- **Chemical Twins:** Due to lanthanide contractions, the properties of elements of 2nd & 3rd transition series are closer, thus pairs of elements possess almost equal atomic size, same valence electrons and very similar properties. They occur together in nature & difficult to separate from one another. Thus these pair of elements is called as chemical twins. Examples are as follows
 - > Niobium & Tantalum: (Nb- 1.34 & Ta- 1.34 Å)
 - > Molybdenum & Tungsten: (Mo 1.29 & W 1.30 Å)
 - **Zirconium & Hafnium:** (Zr 1.45 & Hf 1.44 Å)

Misch Metal:

• From German: *Mischmetall* - "mixed metal". It is an alloy of rare earth elements in various naturally occurring proportions.

- It is also called Cerium Misch Metal, Rare Earth Misch metal Or Misch Metal.
- A typical composition includes approximately 50% Cerium and 25% Lanthanum, with small amounts of Neodymium and Praseodymium. 1-5% Iron or Magnesium.
- Its most common use is in the "flint" ignition device of many lighters and torches, although an alloy of only rare-earth elements would be too soft to give well sparks.
- For this purpose, it is blended with Iron Oxide and Magnesium Oxide to forma harder material known as Ferrocerium.

Preparation of Misch Metals:

- It was prepared from Monazite sand, an anhydrous phosphate of the light Lanthanides and Thorium.
- The ore was "cracked" by reaction at high temperature either with concentrated sulphuric acid or sodium hydroxide (H2SO4/NaOH).
- Thorium was removed, the radioactive Radium isotope were precipitated out using entrainment in Barium Sulphate,
- Remaining lanthanides were converted to the Ln-chloride, was the major commodity chemical of the rare earth industry.
- By careful heating, preferably with Ammonium Chloride or Hydrogen Chloride (NH4Cl/HCl), the hexahydrate could be dehydrated to provide the anhydrous chloride.
- Electrolysis of the molten anhydrous chloride led to the formation of molten Misch metal.

Properties:

- It contains 1-5% Iron. It is pyrophoric i.e. when rubbed against roughsurface, it produces spark
- It melts at about 750°C.

Uses:

- It is used in gas lighter, cigar lighters
- Used for firing mines, signaling, night firing
- Used as powerful reducing agent
- Used in the preparation of flash light powder and in tracer bullets
- Used in metallurgical operations, alloying metals, in Jet Engine parts.

Applications of Lanthanide elements:

- An alloy containing Mg and about 3% misch metal is used in jet engineparts.
- About 15000 ton/year of the lanthanides are consumed as catalysts and in the production of glasses.
- Many technological devices, including Superconductors,
- Sm-Co and Nb-Fe-B high-flux Rare-Earth Magnets,
- Ln-Mg alloys electronic polishers, refining catalysts.
- Hybrid car components (primarily batteries and magnets).
- Used in Optoelectronics applications, most notably the Nd:YAG laser (Neodymium Yttrium Aluminium Garnet; Nd:Y3Al5O12).
- Most lanthanides are widely used in lasers
- Phosphors with lanthanide dopants are also widely used in cathode ray tube

technology such as television sets. The earliest colour television CRTs had a poorquality red; Eu as a phosphor dopant made good red phosphors possible.

- Many defence-related products also use lanthanide elements such as Night Vision Goggles, Rangefinders, the SPY-1 Radar used in some equippedwarships
- Propulsion system of *Raleigh Burke*-class destroyers (Guided Missile Destroyers) all use rare earth elements in critical capacities.
- The price of lanthanum oxide used in Fluid Catalytic Cracking has risenfrom \$5 per kilogram in January 2010 to \$140 per kilogram in June 2011.
- These elements deflect Ultra-Violet and Infra-Red radiation and are commonly used in the production of sunglass lenses.
- La2O3 is used in Crooke's lenses, which give protection from ultra-violet light by absorbing it. CeO2 is used to polish glass.
- Ln-W oxides are improving their high temp properties for welding glass, replacing Th, which was mildly hazardous to work with.
- Erbium-doped fibre amplifiers are significant devices in optical-fibre communication systems.
- Doped-fibre optical amplifiers, Er-doped fibre amplifiers (EDFAs) used as repeaters in the terrestrial and submarine fibre-optic transmission links that carry internet traffic)
- The complex [Gd(DOTA)]- is used in magnetic resonance imaging.

The Actinide series

The series of elements involved in the filling of 5f-orbitals is called actinide series. They follow Ac^{89} and include elements from Th^{90} and Lw^{103} . All isotopes are Radioactive, with only 232Th, 235U, 238U and 244Pu having long half-lives. So the study of their chemistry is difficult in the laboratory. Only Th and U occur naturally occurring, both are more abundant in the earth's crust than tin. The others must be made by Nuclear Processes.

• Actinium: Ac ⁸⁹ :	[Rn] 6d ¹ 7s ²	• Berkelium: Bk ⁹⁷	[Rn]5f ⁹ 7s ²
• Thorium: Th ⁹⁰ :	[Rn]6d ² 7s ²	 Californium: Cf⁹⁸ 	[Rn]5f ^{107s2}
• Protactinium: Pa ⁹¹	[Rn]5f ² 6d ¹ 7s ²	• Einsteinium: Es ⁹⁹	[Rn]5f ¹¹ 7s ²
• Uranium: U ⁹²	[Rn]5f ³ 6d ¹ 7s ²	• Fermium: Fm100	[Rn]5f ^{127s2}
• Neptunium: Np ⁹³	[Rn]5f ⁴ 6d ¹ 7s ²	 Mendelevium: Md101 	[Rn]5f ¹³ 7s ²
• Plutonium: Pu ⁹⁴	[Rn]5f67s2	 Nobelium: No¹⁰² 	[Rn]5f ¹⁴ 7s ²
• Americium: Am ⁹⁵	[Rn]5f77s2	• Lawrencium: Lr ¹⁰³	[Rn]5f ¹⁴ 6d ¹⁷ s ²
nr.			

Position of Lanthanide elements in the periodic table:

The Actinides are belongs to Group IIIA in the 7th period of periodic table. Their actual position is in between Ac^{89} to Rf^{72} . Actinide contraction of trivalent ions is similar to that of the lanthanides, and is caused again by the increasing nuclear charge. The size of atom/cation decreases regularly along the actinides series. The steady decrease in ionic radii with increase in atomic number is referred to as actinide contraction. This is due to poor shielding of 5f-electrons.

T.Y.B.Sc. Chemistry Paper-II Electronic configuration:

The electronic configuration of actinides is not definite. This is due to the complex nature of the electronic spectra. The general electronic configurations of lanthanides are $5f^{2-14}$, $6d^{0/1}$, $7s^{2}$.

- Actinium has electron configuration: La [Rn]⁸⁶, 5f⁰, 6d¹, 7s². It does not possess any 5f electron.
- Thorium also does not possess any 5f electron.
- Protactinium possess in 5f² and 6d¹.
- Uranium possess in $5f^3$ and $6d^1$.
- As the atomic number increases by one i.e. Np⁹³ to Lw¹⁰³, all 14 electrons areenters in the 5f-orbital.
- The valence shell electron configuration of the actinides can be represented as, $5f^2$ to 14, $6d^{0/1}$, $7s^2$.
- The f^0 , f^7 and f^{14} configurations are most stable because empty, half-filled and completely filled orbitals are stable. Thus Ac has empty (f^0), Cu has half-filled (f^7) and Lw has completely filled (f^{14}) orbitals.
- The properties of the actinides and d-block elements are more similar. Many chemical properties of Th, Pa and U are similar to the transition elements. The Ac, Th, Pa and U are exhibit many oxidation state and they are more stable in higher oxidation state.

Oxidation state of the Actinide elements:

Oxidation State +2

- Unusual oxidation state, Common only for the heaviest element
- No^{2+} & Md²⁺ are more stable than Eu²⁺
- Actinide An^{2+} ions have similar properties to Lanthanide Ln^{2+} and to Ba^{2+} ions

Oxidation State +3

- The most common oxidation state
- The most stable oxidation state for all trans-Americium elements
- General properties resemble Ln^{3+} and are size-dependent
- stability constants of complex formation are similar for same size $An^{3+} \& Ln^{3+}$
- An³⁺ & Ln³⁺ separated by ion-exchange/solvent extraction
- Binary Halides, MX3 easily prepared, & easily hydrolysed to MOX
- Binary Oxides, M2O3 known for Ac, Th and trans-Am elements

Oxidation State +4

- Principal oxidation state for Th
- Th⁴⁺ chemistry shows resemblance to Zr^{4+} / Hf^{4+} is it a transition metal?
- Very important, stable state for Pa, U, Pu
- Am, Cm, Bk & Cf are increasingly easily reduced only stable in certain complexes
- Bk⁴⁺ is more oxidizing than Ce⁴⁺
- MO2 known from Th to Cf (fluorite structure)
- MF4 are isostructural with lanthanide tetrafluorides
- MCl4 only known for Th, Pa, U & Np
- Hydrolysis / Complexation / Disproportionation are all important in (aq)

Oxidation State +5

- Principal state for Pa
- Pa^{5+} chemistry resembles that of Nb⁵⁺ / Ta⁵⁺ is it a transition metal?
- For U, Np, Pu and Am the AnO²⁺ ion is known (i.e. quite unlike Nb/Ta)
- Comparatively few other AnV species are known
- e.g. fluorides, PaF5, NbF5, UF5; fluoro-anions, AnF6⁻, AnF7²⁻, AnF8³⁻
- e.g. oxochlorides, PaOCl3, UOCl3; uranates, NaUO3
 Oxidation State +6
- AnO2²⁺ ions are important for U, Np, Pu, Am
- $UO2^{2+}$ is the most stable
- Few other compounds e.g. AnF6 (An = U, Np, Pu), UCl6, UOF4, U(OR)6
 Oxidation State +7
- Only the marginally stable oxo-anions of Np and Pu, e.g. AnO5³⁻

Occurrence of Actinide elements:

The isotopes of elements of ≥ 83 Bi are radioactive. Thus all actinide elements are radioactive. Out of 15 actinides only Actinium, Thorium, Protactinium & Uranium occur naturally (i.e. Z \leq 92). The Actinium &

Protactinium occur only in trace amounts, while Neptunium & Plutonium occur in uranium minerals in minute amounts.

$${}^{238}_{92}U + {}^{1}_{0}n \xrightarrow{239}_{92}U \xrightarrow{\beta}_{23.5 \text{ m}} {}^{239}_{93}Np$$

Most of the longer-lived isotopes decay by β -emission. Half-lives only quantities of 232Th, 235U, 238U, {possibly 244Pu} could have survived since the formation of the solar system. Both Thorium and Uranium are far from rare, they are found in large quantity in earth crust. All remaining actinides are produced synthetically by transformation of naturally occurring elements by nuclear reaction. These synthetic elements are prepared by radioactive decay of Uranium, thus they are called **Transuranic elements**.

Thorium

The Thorium is widely dispersed, accounts for more than >3 ppm of the earth's crust. Natural Thorium is essentially contains 100% 232 Th. It mainly occurs in Monazite [with the rare earths] and in Uranothorite [a mixed Th,U silicate]. The thorium is obtained as ThO2 (thoria) from mineral extraction process. It is used as 99% ThO2 / 1% CeO2 in thoria gas mantles.

Uranium

The natural Uranium is widely distributed and found scattered in the faults of old Igneous Rocks. The Natural Uranium is 99.27% 238U & 0.72% 235U. it is mainly obtained usually as UO2. It is generally used for nuclear fuel, and on a smaller scale for colouring glass/ceramics.

Trans-Uranic Elements:

The actinide elements beyond Uranium synthetically prepared by nuclear reaction are

Chemistry of F-block element

called **Transuranic elements.** These are elements from 93Np to 103Lw. These elements are not found in nature and they are synthetically prepared by nuclear reactions.

Nuclear particles: Neutrons- 10η , Proton- 11H, Electron- e^{-1} , Deuterons-21D1, Triton- $31T_2$, +Beta- $0_{-1\beta}$, -Beta- $0_{+1\beta}$, γ - high Energy, α -particles- $42He_2$, Carbon $12_{6}C$,

Preparation of Transuranic elements:

There are 3 methods for preparations of transuranic elements such as...

- a) Neutron bombardment
- b) Accelerated particle bombardment
- c) Heavy ion bombardment

a) Neutron bombardment

This process carried out in nuclear reactor. The **neutron is capture** by nucleus & becomes **unstable**. Then neutron is converted into proton, and then followed by β emission. It gives element with higher atomic number by one unit.



Thus the process of synthesis of transuranic elements involves capture of successive neutrons by (η, γ) to produces elements with higher atomic number.



Theoretically, the synthesis of new elements can be continued until the neutron/ proton ratio of the daughter element is too high to have a stable existance.

The yield of the heavier member is controlled by two factors:

- i. The half life of the isotopes.
- ii. By its ability to absorb neutron.

Chemistry of F-block element

The most important neutron reactions are $(\eta, \gamma)(\eta, \alpha)(\eta, \rho)(\eta, \gamma)(\eta, 2\eta)(\eta, \gamma)(\eta, 2\eta)(\eta, \gamma)(\eta, \gamma)(\eta,$ 5η)(η , 6η)(η , fission). The first symbol in the bracket represents the bombarding particle and the other symbol for the type of energy liberated or the nature of the particlr eliminated in the neutron reaction.

b) Bombardment with Accelerated particles or High voltage Nuclei :

The synthesis of transuranic elements carried by using Accelerated projectile (bombarding particles) such as alpha 42He, proton ¹1P, deuterium ²1D. In this process nucleus captures the lighter particles and produces new elements of higher atomic number. The important projectile particles and their reactions are may be (α,η) , $(\alpha,2\eta)$, $(\alpha,3\eta)$, $(\alpha,5\eta)$, (\mathbf{D},η) , $(D,2\eta)(D,3\eta)$, etc.

239 _{Pu} (241 _{Cm} 94	α,2η) 96	241 _{Cm (α,2η)} 2 96 98	44 _{Cf}
235 _{U (I}	<u> </u>	238 _{U (D,2η)} 23	38 _{Np}
236 _{Np}	02	92 93	
92	93	U	
R			

$$\begin{array}{cccc} 238_{\mathrm{U}} _{(\alpha,5\eta)} & 237_{\mathrm{Pu}} \\ 92 & 94 \\ & &$$

a) Heavy ion bombardment

This is modern technique for the synthesis of transuranic elements. Heaviestelements are made by capturing the nuclei heavy ion bombardment. The heavy ions used are such as **94Be**, **126C**, **147N**, **168O**. This process carried out in nuclear reactor. The heavy ion particles are bombarded on target element; it receives more mass and charge. It is then releases same neutron.



Many of the transuranic elements have now been made with indifferent isotopic forms. Following reactions indicate the formation of only one of the possible isotopes. Many of them are exceedingly short live.





Nuclear Fuels and Their Applications

Wood material is used as fuel for obtaining energy, but coal is very poor source because it releases small percentage of energy. The petroleum is superior source than wood. While nuclear fuels are different from all traditional energy sources. The energy obtained from nucleus of an atom from which million times more energy obtained than the chemical energy.

The Einstein's equation is famous for the conversion of Mass into Energy,

i.e. $E = MC^2$; where M = Mass (Kg), C = Speed Of Light, $C = 2.998 \times 10^8$ M/S. The energy may be released in the form of light, radiation, kinetic energy and heat. The very large quantity of energy (about 10^{12} cal) by fusion of hydrogen atoms into helium as well as enormous energy (about 200MeV) released by breaking of Uranium nucleus into smaller nucleus. Fission and Fusion reactions are highly exothermic (1 Mev / nucleon). This is 10⁶ times larger than "chemical" reactions which are about 1 ev / atom. Nuclear fission was first used in a chain reaction:

²³⁵U₉₂ + ${}^{1}n_{0}$ \longrightarrow ¹³⁹Ba₅₆ + 94 Kr₃₆ + 3 ${}^{1}n_{0}$ +200 MeV (or 10¹⁰ kJ mol⁻¹) Or ²³⁵U₉₂ + ${}^{1}n_{0}$ \longrightarrow ¹³⁸I₅₃ + 95 Y₃₉ +3 ${}^{1}n_{0}$ +2 × 10¹⁰ jK mole⁻¹

Large amount of energy is released during this fission reaction is about 200MeV or 10^{10} KJ/Mol.

Electron volt (ev): The energy an electron acquires when it moves through a potential difference of one volt:

 $1 \text{ ev} = 1.602 \text{ x} 10^{-19} \text{J}$

Binding energies are commonly expressed in units of mega electron volts (Mev)1 Mev

 $= 10^{6} \text{ ev} = 1.602 \text{ x} 10^{-13} \text{J}$

A particularly useful factor converts a given mass defect in atomic mass units to its energy equivalent in electron volts:

 $1 \text{ amu} = 931.5 \text{ x } 10^6 \text{ ev} = 931.5 \text{ Mev}$

Nuclear fuels can be defined as, 'the element which produces heat energyby its nuclear fission or fusion'. The Nuclear power is the 4th largest source of electricity in India after thermal, hydroelectric and renewable sources of electricity. As of 2010, India has 20 nuclear reactors in operation, generating 4,780 MW while 7 other reactors are under construction and are expected to generate an additional 5,300 MW. The first commercial nuclear power stations started operation in the 1950s. In October 2010, India drew up "an ambitious plan to reach a nuclear power capacity of **63,000 MW in 2032**"

There are now over 700 commercial nuclear power reactors operating in 30 countries, with 377,000 MW energy of total capacity. They provide about 14% of the world's electricity as continuous, reliable base-load power, and their efficiency is increasing. About 56 countries operate a total of about 250 research reactors and a further 180 nuclear reactors power some 140 ships and submarines.

There are two types of nuclear fuels such as Nuclear Fusion fuels and Nuclear Fission fuels.

Nuclear Fusion fuels:

The fusion of two lighter nuclei yields a more stable nucleus and an enormous amount of energy is released. The fusion of four hydrogen nuclei into helium atom was result in the liberation of large amount of energy. These type of reactions are possible only at very higher temperature.

```
2H+3H\rightarrow 4He+\frac{1}{0}n+18.38MeV
```

Same type of reactions are occurs in hydrogen bomb explosion. The principle of hydrogen bomb is based on fast conversion of hydrogen into helium. This process of nuclear fusion reactions also the source of hydrogen burning and helium burning reaction found on stars.



Hydrogen Burning in Stars and Fusion Reactions

Chemistry of F-block element

 $2_{\rm H} + 3_{\rm He} \rightarrow 4_{\rm He} + 1_{\rm H} + 18.3 \text{ Mev}$ $2_{\rm H} + 3_{\rm H} \rightarrow 4_{\rm He} + 1_{\rm n} + 17.6 \,{\rm Mev},$

This is Easiest nuclear reaction!

Helium "Burning" Reactions in Stars

 $\begin{array}{r} 16_{\rm O} + 4_{\rm He} \rightarrow 20_{\rm Ne} \\ 24_{\rm Mg} + 4_{\rm He} \rightarrow 28_{\rm Si} \end{array}$ $12_{\rm C} + 4_{\rm He} \rightarrow 16_{\rm O}$ $20_{\text{Ne}} + 4_{\text{He}} \rightarrow 24_{\text{Mg}}$ $32_{\text{S}} + 4_{\text{He}} \rightarrow 36_{\text{Ar}}$ $28_{\text{Si}} + 4_{\text{He}} \rightarrow 32_{\text{S}}$ $36Ar + 4He \rightarrow 40Ca$

Advantages of Nuclear Fusion Fuels:

- It is very cheap and readily available hydrogen, deuterium and tritiumwould be used as source of fusion fuels.
- There will be no any problem of the disposal of radioactive products as it is form by fission products.
- There will be no danger of exhausting raw materials.
- The quantity of naturally occurring uranium is decreases now a day.

Nuclear fission fuels:

1 Mole of 235U (about 1/2 lb) produces 2 x 10^{10} kJ which is equivalent to the combustion of 800 tons of Coal! Commercial nuclear reactors use fission to produce electricity. Same nuclear Fission reaction ["atomic bombs"] was used in the destruction of Hiroshima and Nagasaki, Japan, in August 1945.

When 235U is bombarded with one neutron, then uranium atom is splits into two lighter nuclei of nearly equal mass and the change is accompanied by the release of large amount of energy. This phenomenon has been called as nuclear fission.

 $235_{\text{U}} + 1_{\text{n}} \rightarrow 141_{\text{Ba}} + 92_{\text{Kr}} + 3 1_{\text{n}} + 200 \text{ Mev},$

The process of splitting of larger nuclei into two approximately into two equalparts is called Fission reaction. During each stage on accepting of one neutron; three neutrons are liberate with large energy. The Fission Chain Reaction proceeds geometrically: 1 neutron \Box 3 \square 9 \square 27 \square 81... etc \square When neutron liberation is uncontrolled, and then this spontaneous reaction gives explosion with high temperature. This is called chain reaction and it is mechanism of nuclear bomb. Only three isotopes of the heavy elements i.e. 233U, 235U, and ²³⁹Pu are suitable for fission reaction and hence these three elements are called as nuclear fuels. Out of three fissionable isotopes only ²³⁵U, is occurs in nature as a one part in 140 partsof natural ²³⁸U. Other two are produced artificially by nuclear reaction as follows...

1. Use of **233**U

92

This isotope of Uranium is not occurs in nature. It is fissionable, stable and has long half-life period of 1.6 X10⁵ years. It is obtained by nuclear reaction from ²³²Th material.

$$\begin{array}{ccc} 232_{\rm Th} (\eta, \gamma) & 233_{\rm Pu} \\ 90 & 90 \end{array}$$

$$\begin{array}{ccc} 233_{\rm Pa} (\beta^{-}) & 233_{\rm U} \\ 91 & 92 \end{array}$$

92

The isotope ²³³U undergoes fission reaction and produces large amount ofenergy. Thus 233U is called as nuclear fuels.

 $233U + 1n \rightarrow 139Ba + 92Kr + 3 1n + 200 Mev$

2. 239_{Pu}

94

This isotope of Plutonium can be radially separated chemically from Uranium residue of nuclear reactor. It is fissionable like 235 U, stable and has long half-life period of 24360 years. It is obtained by nuclear reaction from 238 U material.

The natural ²³⁸U and ²³²Th are **fertile materials** and they are converted into ²³⁹Pu and ²³³U called **fissile material**.

IUPAC Nomenclature system for super heavy elements with atomic number greater than 100:

Elements of atomic numbers greater than 100 are often referred to in the scientific literature but receive names only after they have been 'discovered'. The Names are needed for indexing and other purposes. Thus the Commission on Nomenclature of Inorganic Chemistry was asked to make recommendations concerning names and symbols of the heavy 'unknown' elements. The Commission decided that these elements would be best named systematically and that names should accord with the following principles:

Principles of Nomenclature:

- 1. The names should be short and obviously related to the atomic numbers of the elements.
- 2. The names should end in 'ium' whether the element was expected to be ametal or otherwise.
- 3. The symbols for the systematically named elements should consist of threeletters.
- 4. The symbols should be derived directly from the atomic numbers and bevisually related to the names as far as possible.

The Nomenclature Rules:

1. The name is derived directly from the atomic number of the element using the following numerical roots:

0 = nil, 1 = un, 2 = bi, 3 = tri, 4 = quad, 5 = pent, 6 = hex, 7 = sept, 8 = oct and 9 = enn.

- 2. The roots are put together in the order of the digits which make up the atomic number and **terminated by 'ium'** to spell out the name. The final 'n' of 'enn' is elided when it occurs before 'nil', and the final 'i' of 'bi' and of 'tri'
- 3. when it occurs before 'ium'.
- 4. The symbol of the element is composed of the initial letters of the numerical roots which make up the name.
- 5. The root 'un' is pronounced with a long 'u', to rhyme with 'moon'. In the element names each root is to be pronounced separately.

Chemistry of F-block element

Atomic	Namo	Symbol				
number	Name	Symbol	130	Untrinilium	Utn	
101	Mendelevium	Md*	140	Unquadnilium	Uqn	
	(Onnitunium)		150	Unpentnilium	Upn	
102	(Unnilbium)	No*	160	Unhexnilium	Uhn	
	Lawrencium		170	Unseptnilium	Usn	
103	(Unniltrium)	Lr*	180	Unoctnilium	Uon	
104	Unnilquadium	Unq	190	Unennilium	Uen	
105	Unnilpentium	Unp				
106	Unnilhexium	Unh	200	Binilnilium	Bnn	
107	Unnilseptium	Uns	201	Binilunium	Bnu	
108	Unniloctium	Uno	202	Binilbium	Bnb	
109	Unnilennium	Une	202	biiiibiuiii		
110	Ununnilium	Uun				
111	Unununium	Uuu	300	Trinilnilium	Tnn	
112	Ununbium	Uub	400	Quadnilnilium	Qnn	
113	Ununtrium	Uut	500	Pentnilnilium	Pnn	
114	Ununquadium	Uuq				
115	Ununpentium	Uup	900	Ennilnilium	Enn	

Comparison between Nuclear Fission and Fusion Reaction

	Nuclear Fission	Nuclear Fusion
Definition:	Fission is the splitting of a large atom into two or more smaller ones.	Fusion is the fusing of two or more lighter atoms into a larger one.
Natural occurrence:	Fission reaction does not normally occur in nature.	Fusion occurs in stars, such as the sun.
By products of reaction:	Fission produces many highly radioactive particles.	Few radioactive particles are produced by fusion reaction.
Conditions:	Critical mass of substance and high-speed neutrons are required.	High density, high temperature environment is required.
Energy Requirement:	Takes little energy to split two atoms in a fission reaction.	Extremely high energy is required to bring two or more protons close.
Energy Released:	The energy released by fission is a million times greater than that released in chemical reactions, but lower than the energy released by nuclear fusion.	The energy released by fusion is three to four times greater than the energy released by fission.
Nuclear weapon:	Nuclear weapon is a fission bomb, also known as an atomic bomb or atom bomb.	Nuclear weapon is the hydrogen bomb, which uses a fusion reaction.

Elements with even number of protons in the nucleus (even atomic number) are generally more stable than their neighbors with odd atomic numbers. This is called **Herkin's Rule**. It states that " elements with an even atomic number (i.e an even number of protons in the nucleus) are more abundant than their neighbours eith odd atomic numbers".

Property	Lanthenides	Actinides
1.Position in	i. Belong to sixth period	i. Belong to seventh period and four
periodic table	and transition series. It	transition series. It constitutes second
1	constitutes first inner	inner transition series.
	transition series.	i. Except uranium and thorium all othe
2.Occurrence	Except promethium,	prepared synthetically. Only thoriu
	all occur in nature	and uranium occur in nature abundantly
	abundantly	
3.Electron	i. Differentiating	i. Differentiating electron enters
configuration	electron enters 4f	5f orbitals.
	orbitals.	ii. Filling of 5f level is not so
	ii. Filling of 4f level	regular.
	is regular.	iii. 5f electrons are not so deeply
	iii. 4f electrons are	buried in their atoms or ions.
	deeply buried in	
	their atoms or ions.	
4.Radioactive	Only promethium is	Majority of these elements are
nature	radioactive.	radioactive
5. Bonding	The 41 orbitals do	The SI orbitals can and do take
	hot take part in bonding Hence they	covalent band
	form ionic bond	covarent bond.
6 Complex	They do not have	They have strong tendency to
formation	much tendency to	form complexes
	form complexes.	
7. Spectra	Absorption spectra	Absorption spectra consists of
1	consists of narrow	narrow bands but are about 10
	and sharp bands.	times as intense as the lanthanide
		bands.
8.Oxidation	Show only $+2$, $+3$	Show a wider range of oxidation
states	and +4 oxidation	states such as +2 to +7 e.g. +5
	states	state in NpO ₂ and +6 in the UO ₂ $^{2+}$
XY		ion.
×		

CH-3⁄42

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