LESSON -I ELECTRONIC CONFIGURATION AND OXIDATION STATES OF LANTHANIDES AND ACTINIDES.

Objectives – Position in the periodic table – Electronic configuration of Lanthanides and actinides – Oxidation states

1.1.i) Introduction:

The lanthanides sometimes called as Lanthanones are the first inner transition elements. The fourteen elements after lanthanum i.e. from cerium to lutetium (At.No.58-71) are the lanthanides. In this 4f orbitals are filled.

The Actinides are the second inner transition elements. The fourteen elements after actinium i.e., from thorium to lawrencium (At.No.90-103) are actinides. In this 5f orbitals are filled.

The lanthanides are characterized by gradual filling of the 4f sub shell and the actinides by filling of the 5f sub shell.

1.1.ii) Position in the periodic table:

Lanthanides and actinides are generally named as inner transition elements because they constitute transition series within d-block elements. These are also called as f-block elements. 4f series are lanthanides and 5f series are actinides.

Group three elements are

Element		Electronic configuration
Scandium	Sc	$[Ar]\ 3d^1\ 4s^2$
Yttrium	Y	$[Kr]\ 4d^1\ 5s^2$
Lanthanum	La	$[Xe]\ 5d^1\ 6s^2$
Actinium	Ac	$[Rn]\ 56^1\ 7s^2$

These four elements are sometimes grouped with the 14 lanthanides and called collectively the **'rare earths'**. This is a minomer because the scandium groups are d-block elements and the lanthanides are f-block elements.

In the d-block (transition elements) next to scandium group are

Titanium	Ti	[Ar] $3d^2 4s^2$
Zirconium	Zr	[Kr] $4d^2 5s^2$
Hafnium	Hf	[Ze] $5d^2 6s^2$
Dubinium (104)		[Rn] $6d^2 7s^2$

The lanthanides lies in between La (57) and Hf (72) i.e,. in the transition elements (d-block elements). So these are called first inner transition series. The actinides lies in between Ac (89) and Dubinium (104), so second inner transition series. Because these lanthanides and actinides position in the periodic table is in the transition series and in between two transition elements, they are named as inner transition elements. To understand the position in the periodic table we start with configuration of Xe (At.No.54).

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$$

At Xe, the 6s and 6p-orbitals become stable. Since these orbitals are more penetrating, so Z(effective nuclear charge) is greater and thus lower the energy.

Further addition of electrons in 6s gives alkali metal, Cs and a rare earth element Ba. At Ba all the three sub shells –6s,5d and 4f have very similar energies. In lanthanum the electron enters 5d orbital and its configuration is [Xe] $4f^0 5d^1 6s^2$. As we move further, the 4f sub shell becomes more stable than 5d-subshell and therefore the next electron in Ce enters in 4f –sub shell, [Xe] $4f^2 6s^2$. The filling of 4f continues till Lu (71), [Xe] $4f^{14} 5d^1 6s^2$ with which the lanthanides ends. From the next element Hf onwards, the 5de electrons are filled (d-block of transition element). The Hf (At.No.72), [Xe] $4f^{14} 5d^2 6s^2$.

The general formula of lanthanides or actinides is $(n-2)f^{1-14} (n-1)d^{0-1} ns^2$. The position of lanthanides is shown in Fig 1.1.

THE PERIODIC TABLE

Subshells being completed

ns — (*n*−1)*d* — *np*

Nonmetals

Light metals — Transition metals — Posttransition metals

Principal quantum number *n*

1	1 H	2 He																
"American" →	I A	II A											III A	IV A	V A	VI A	VII A	VIII A
"1–18" →	(1)	(2)											(13)	(14)	(15)	(16)	(17)	(18) 2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
			III B	IV B	V B	VI B	VII B	VIII B			I B	II B						
3	11 Na	12 Mg	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	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 (Unq)	105 Ha (Unp)	106 Unh	107 Uns	108 Uno	109 Une									

(*n*−2)*f*

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
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

1.1.iii) Electronic configuration of lanthanides.

The elements, atomic number, electronic configuration and physical state of the first inner transition series are given in table 1.1

Table 1.1.

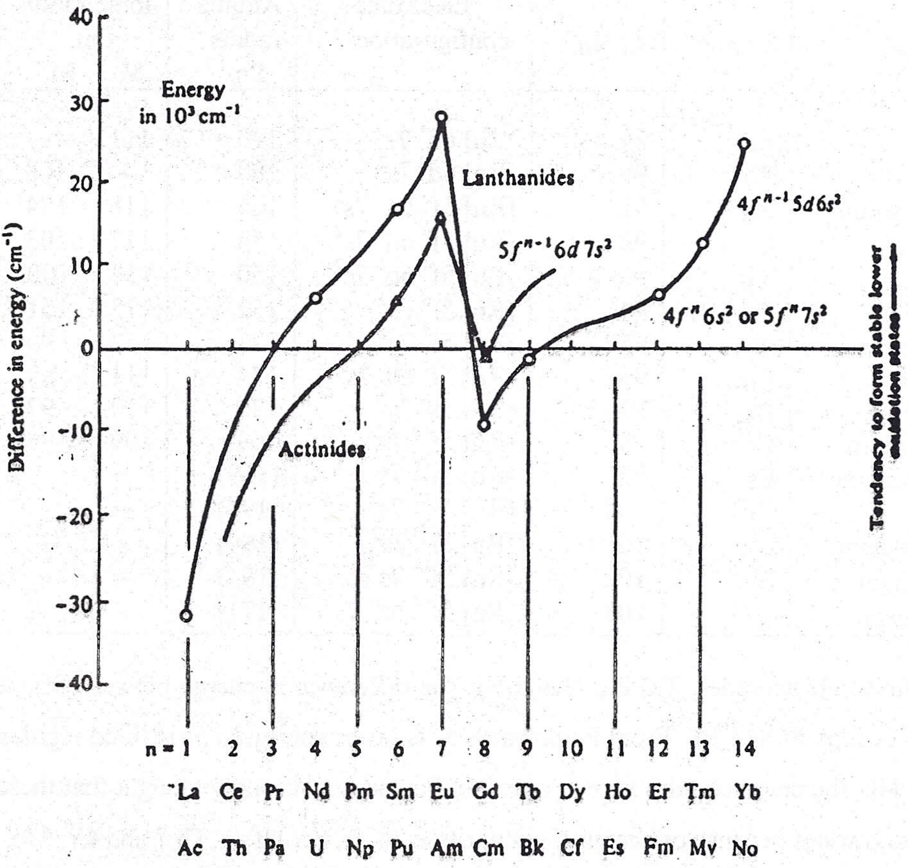
Electronic configuration and physical data of lanthanides.

Element	Symbol	At.No.	Electronic Configuration	Atomic radius (pm)	Ionic radius (pm)M^{3+}	M.P. ^0C	Density/ $gm.cm^{-3}$
Lanthanum	La	57	[Xe] $5d^1 6s^2$	187	115	920	6.15
Cerium	Ce	58	[Xe] $4f^1 5d^1 6s^2$	183	111	795	6.78
Praseodymium	Pr	59	[Xe] $4f^3 6s^2$	182	109	935	6.78
Neodymium	Nd	60	[Xe] $4f^4 6s^2$	181	108	1020	7.00
Promethium	Pm	61	[Xe] $4f^5 6s^2$	-	106	1030	-
Samarium	Sm	62	[Xe] $4f^6 6s^2$	179	104	1070	7.54
Europium	Eu	63	[Xe] $4f^7 6s^2$	204	112	826	5.24
Gadolinium	Gd	64	[Xe] $4f^7 6d^1 6s^2$	180	102	1310	7.95
Terbium	Tb	65	[Xe] $4f^9 6s^2$	178	100	1360	8.27
Dysprosium	Dy	66	[Xe] $4f^{10} 6s^2$	177	99	1410	8.56
Holmium	Ho	67	[Xe] $4f^{11} 6s^2$	176	97	1460	8.80
Erbium	Er	68	[Xe] $4f^{12} 6s^2$	175	96	1500	9.16
Thulium	Tm	69	[Xe] $4f^{13} 6s^2$	174	95	1540	9.33
Ytterbium	Yb	70	[Xe] $4f^{14} 6s^2$	194	94	824	6.98
Lutetium	Lu	71	[Xe] $4f^{14} 5d^1 6s^2$	174	93	165	9.84

a. Only the valence shell electrons i.e,. those outside the [Xe] shell are given.

b. pm – in picometers.

It might be expected that 14 elements from Ce to Lu would be formed by adding 1,2…14 electrons in 4f level. It is energetically favorable to move single 5d electron to 4f level. It is energetically favorable to move single 5d electron to 4f level in most of the elements. The relative energies of the nd and (n-1)f orbitals are very similar and sensitive to the occupancy of these orbitals and are shown in Fig 1.2



page 1.5

Approximate relative energies of the f^{n-1} and $f^n s^2$ election Configuration

1.1.iv) Electronic configuration of actinides.

The elements, atomic number, electronic configuration and physical data of the second inner transition series are given in table 1.2.

Table 1.2.

Electronic configuration and physical data of actinides.

Element	Symbol	At.No.	Electronic configuration	Atomic radius Pm	Ionic radius Pm		M..P. 1^0C
					M^{3+}	M^{4+}	
Actinium	Ac	89	[Rn] $6d^1\ 7s^2$	190	111	-	1050
1.Thorium	Th	90	[Rn] $6d^2\ 7s^2$	180	-	108	1750
2. Protactinium	Pa	91	[Rn] $5f^2\ 6d^1\ 7s^2$	164	118	104	1572
3. Uranium	U	92	[Rn] $5f^3\ 6d^1\ 7s^2$	154	117	103	1132
4. Neptunium	Np	93	[Rn] $5f^4\ 6d^1\ 7s^2$	150	114	100	639
5. Plutonium	Pu	94	[Rn] $5f^6\ 7s^2$	152	115	101	640
6. Americium	Am	95	[Rn] $5f^7\ 7s^2$	173	112	99	1173
7. Curium	Cm	96	[Rn] $5f^7\ 6d^1\ 7s^2$	174	111	99	1350
7. Berkelium	Bk	97	[Rn] $5f^9\ 7s^2$	170	110	97	986
9. Californium	Cf	98	[Rn] $5f^{10}\ 7s^2$	169	109	96	900
10. Einsteinium	Es	99	[Rn] $5f^{11}\ 7s^2$	(169)	-	-	-
11.Fermium	Fm	100	[Rn] $5f^{12}\ 7s^2$	(194)	-	-	-
12.Mendelevim	Md	101	[Rn] $5f^{13}\ 7s^2$	(194)	-	-	-
13. Nobelium	No	102	[Rn] $5f^{14}\ 7s^2$	(194)	-	-	-
14. Lawrencium	Lr	103	[Rn] $5f^{14}\ 6d^1\ 7s^2$	(171)	-	-	-

For the first four actinides, Th, Pa, U and Np, the difference in energy between 5f and 6d is small. So electrons occupy 5f and 6d. From Pu onwards 5f is lower energy so 5f is filled regularly.

Before 1940, the only actinides known were Th, Pa and U. Wrongly thought that these were belongs to d series because of chemical similarity with Ti, Zr, Hf ….Th ? and Cr, Mo, W,….U ?. Increase in number of oxidation states, increased stability of higher states as found in d-block. This is in contrast to +3 uniform oxidation state in lanthanides. Man made artificial elements have At. No higher than U – 92 (Trans uranium elements Np – Lw). After this,, the actinides are considered as f-block elements. After the actinide elements i.e,. lawrencium, the discovered elements, are d-block elements because in them the 6d level is filled gradually like in the 3rd transition series 5d is filled. The elements 122,123,124----if at all discovered, they can be named as super actinides. The discovered elements 103 are

Dubnium – 104	Joliotium – 105	Rutherfordium – 106
Bohrium – 107	Hahnium – 108	Meitnerium - 109

1.1.v) Oxidation states of Lanthanides and Actinides.

a) Oxidation states of lanthanides.

Ln symbol is used for lanthanides. +3 state is stable for all lanthanides so they resemble closely, the other oxidation states occur are +2 and +4 for lanthanides to obtain

1) a nobel gas configuration eg. Ce^{4+} $[Xe]\ 4f^0$
2) half filled f shell Eu^{2+} Tb^{4+} $[Xe]\ 4f^7$.
3) completely filled f shell Yb^{2+} $[Xe]\ 4f^{14}$.

In addition, +2 and +4 exists for those elements that are close to these states. For eg.,

Sm^{2+} $[Xe]\ 4f^6$ and Tm^{2+} $[Xe]\ 4f^{13}$

Pr^{4+} $[Xe]\ 4f^1$ and Nd^{4+} $[Xe]\ 4f^2$

Higher oxidation states occur in fluorides and oxides and lower oxidation states in the other halides like, Br^-, I^-.

The characteristic +3 oxidation state of lanthanide elements together with the notable similarity in size made difficulty in the separation of these elements prior to the development of chromatographic methods. The 4f orbitals are well shielded by 5s and 5p, the 4f electrons do not loose to give the variable oxidation states.

b) Oxidation states of actinides.

Actinides (An) all have an oxidation state of +3 like lanthanides but this is not most stable like in Ln^{3+}. The different oxidation states of actinides are given in Table 1.3

Table 1.3

Oxidation states of the actinide elements.

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
-	-	-	-	-	-	2c	-	-	2d	2d	2d	2d	2d	-
3a	3b	3	3	3	3	3a	3a	3a	3a	3a	3a	3a	3a	3a
-	4a	4	4	4	4a	5	4	4	-	-	-	-	-	-
-	-	5a	5	5a	5	6	-	-	5	-	-	-	-	-
-	-	-	6	6	6	6	-	-	-	-	-	-	-	-
-	-	-	-	7	7	-	-	-	-	-	-	-	-	-

a. Most stable.

b. Solid-state only

c. In CaF_2 lattice

d. So far only in solution.

For Th, Pa, U and Np +3 state is not stable and except these, the other actinides have +3 sable state and properties are similar to Ln.

The most stable state for Th is +4, Pa is +5, U is +6, Np is +5

Plutonium shows all oxidation states from +3 to +7, but Pu^{4+} is stable.

Neptunium shows all oxidation states from +3 to +6 but Np^{5+} is stable.

The lower oxidation states are tend to be ionic and higher oxidation states are tend to be covalent.

The actinides, in contrast to lanthanides, utilize their f electrons more readily and thus exhibit oxidation states equal to the sum of the 7s, 6d and 5f electrons. As in the first transition series, this trend reaches maximum at +7 i.e. at plutonium and there after there is a tendency toward lower oxidation states (see table 1.3). A reduced tendency to use 5f electrons as one progress along actinide series is apparent.

1.1.vi) Model questions.

1. Write the names and electronic configuration of lanthanide elements. Why the anemoly in the configuration ?
2. What are the different oxidation states lanthanide elements, give reasons for attain [illegible] and +4 oxidation states?
3. Name the discovered transactimide elements or fourth transition elements?
4. Write the names and electronic configuration of IInd inner transition elements?
5. Why the lanthanides and actinides are named as inner transition elements?
6. Name the transuranic elements in the configurations?
7. Why there are variable oxidation states in actinides like in transition elements and why not is the lanthanide?
8. What are different oxidation states exhibited by actinides?
9. Discuss about the position of lanthanides and actinides in the periodic table?

1.1.vi) Recommended book.

1. F.A.Cotton and G.Wilkinson.	Advanced Inorganic Chemistry.
2. J.E. Huhey	Inorganic Chemistry.
3. J.D.Lee	Concise Inorganic Chemistry.
4. G.F. Lipport	Modern Inorganic Chemistry.
5. Gurdeep raj	Advanced Inorganic Chemistry

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LESSON-II SEPARATION METHODS OF LANTHANIDES AND ACTINIDES.

Objectives – Occurrence of lanthanides – Processing the mineral Methods of separation of lanthanides – Synthesis of transuranium elements – Methods of separation of actinide elements.

1.2.i) Introduction

As early as 1794, the Sweedish chemist Gadolin announced the discovery of an oxide which he named yttria and it was not until about fifty years later that this so called substance was broken down into three portions named yattria, erbia and terbia. Over the years further separations were achieved, including the isolation of an oxide called lutetia. Of course the names of the lanthanides as we now know them are obtained by changing the ending - a in the oxide into – um e.g., yttria changes to yttrium.

The major source of the lanthanides is monazite sand which is composed chiefly of the phosphate of thorium, cerium, neodymium and lanthanum; the phosphate portion of monazite contains small traces of other lanthanide ions, and the only lanthanide that does not occur naturally is promethium, which is made artificially by nuclear reactions.

Prior to 1940 only the first four members of actinides were known, namely-actinium, thorium, protactinium and uranium. The discovery of the first transuranium element neptunium dates back to 1940, the formation of the others following at fairly regular intervals and culminating the identification of lawrencium in 1961. This actinide series of elements were basically similar to lanthanides helped in the identification of further transuranium elements.

1.2.ii) Occurrence of lanthanides.

The lanthanides are named as rare earths. The important minerals of lanthanides are given in table 1.4.

Table 1.4.

Important minerals of lanthanides

Minerals	Composition	Location of significant deposits
1. Monazite sand – mixture of orthophosphates of Ce – earths. $CePO_4$	50-70% Ce-earths (At.No.57-62 calculated as oxides) 1-4% Y-earths (At.No.63-71 calculated as oxides) 5-10% ThO_2 1-2% SiO_2 22-30% P_2O_5 Traces of U	Occurs in sand beaches of Travancore. Brazil, South Africa,
2. Bastaesite – Cerium earth fluorocarbonate $CeFCO_3$	65-70% Ce-earth < 1% Y-earths	Sweden, California New Mexico
3. Cerite – hydrated silicate $Ce_3M^{11}H_3Si_3O_{11}$(M-Ca,Fe).	51-72% Ce-earths 7.6% Y- earths Traces of Th U, Zr.	Sweden
4. Gadolinite or Yetterbite $(Fe,Be)_3(Y)_2Si_2O_{10}$	35-48% Y-earths, 2-17% Ce-earths 11.6% BeO.	Sweden, Norway USA (Texas)
5. Xenotime – YPO_4	54-65% Y-earths ~0.1% Ce – earths 3% ThO_2, 3.5% U_3O_8, 2-3% ZrO_2	Norway, Brazil.
6. Euxenite – $Y(Nb,Ta)TiO_6$. H_2O.	13-35% Y-earths, 2-8% Ce-earths, 20-30% ThO_2, 25-30% $(Nb,Ta)_2O_5$	Australia, Idaho

1.2.iii) Extraction and separation of lanthanides.

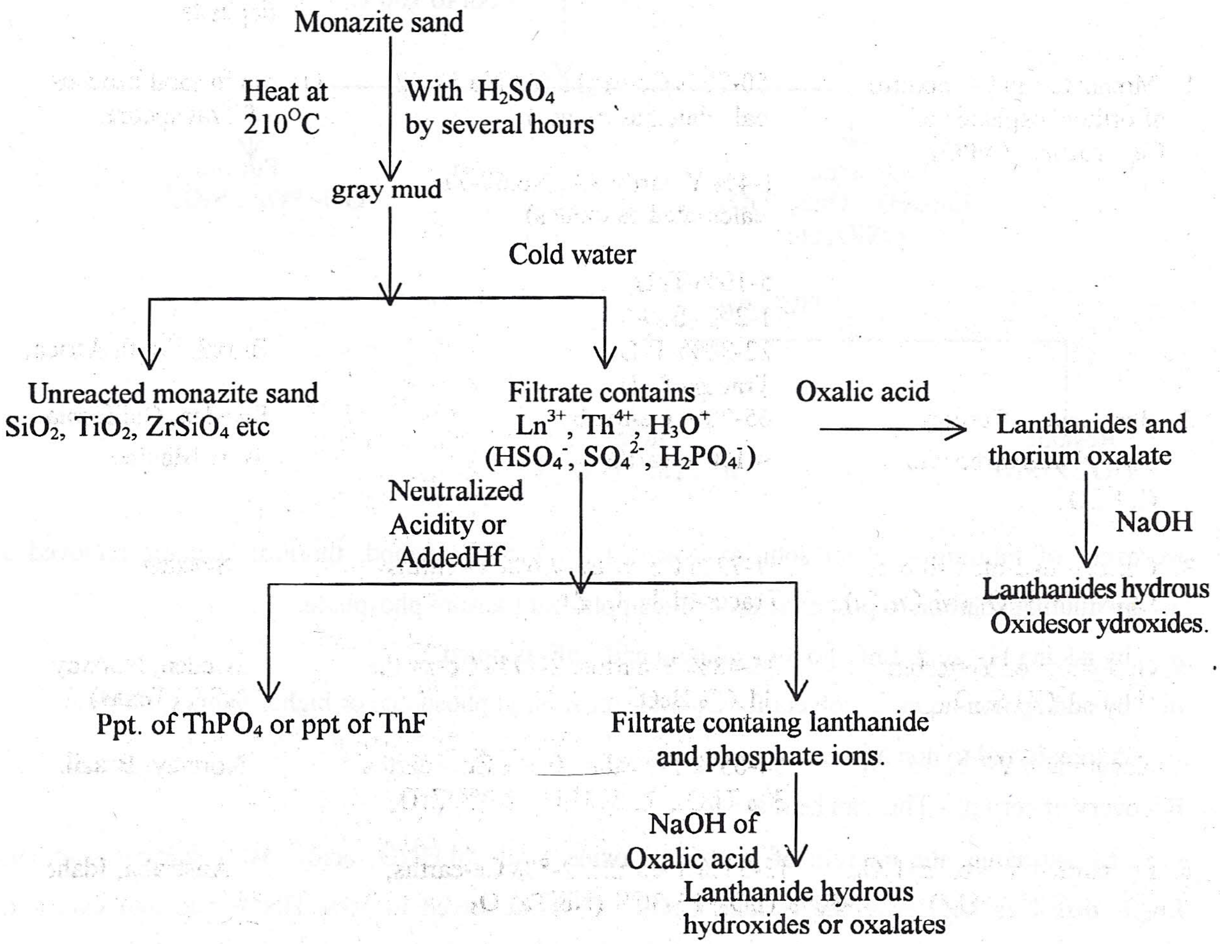
a) PROCRESSING THE MINERAL

Processing amount to cracking the mineral, recovering lanthanides, removing thorium if present, and separating the lanthanides. It is ordinarily.most convenient to remove cerium before fractionating the other lanthanides. Monazite my be cracked by two methods.

1) Sulphuric acid method:

Monazite is digested with sulphuric acid at elevated temperature for several hours to give mix of sulphates containing phosphoric acid. The whole process is outlined below in the flow sheet -1.

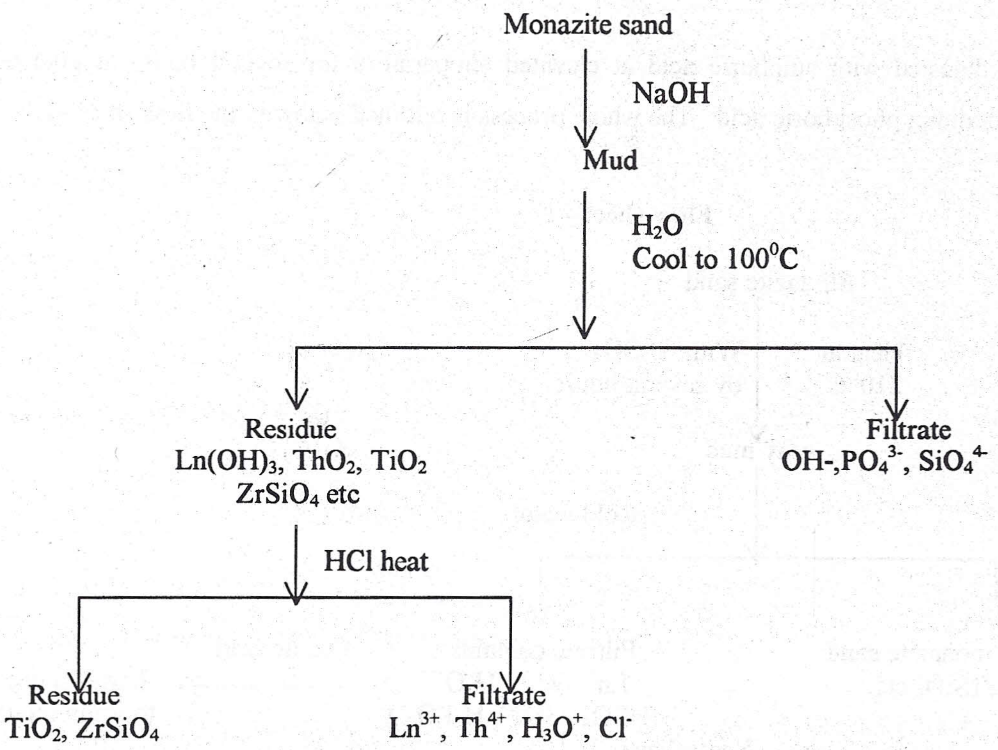
Flow sheet - 1



2) Sodium hydroxide method:

Monazite sand is heated at about 140°C with 73% sodium hydroxide. The various steps in the process can be summarized in flow sheet –2.

Flow sheet – 2



Recovery of thorium – From solution obtained by 1 or 2 method, thorium can be removed as-

i. by diluting solution to proper acidity which ppts. out thorium phosphate.

ii. by adding HF acid, LnF_4 go into solution and ThF_4 is ppted.

iii. by adding non-aqueous solvent for example ter-n-butyl phosphate or higher amines, thorium is transferred to non.aq.solvent.

Recovery of cerium - This can be done

i. by extracting the mixture of lanthanide oxides with dil.HNO_3 acid. More basic sesquioxides Ln_2O_3 dissolves and leave the residue CeO_2. CeO_2 dissolved in 85% HNO_3 and add excess dil. H_2SO_4, Ce is ppt.as $Ce(OH)(NO_3)_3 \cdot 3H_2O$.

b). Separation of lanthanides –

Separation of lanthanide hydroxides or lanthanide oxalates in the above methods may be effected by one or another or some combination of the following general procedures-

1) Fractional crystallization of isomorphous salts

2) Basicity differences

  a) fractional precipitation
  b) fractional thermal decomposition of salts
  c) ion exchange
  d) solvent extraction
3) selective oxidation and reduction
4) physical differences

i. Ion Exchange method

Ion exchange is the reversible interchange of ions of similar charge furnished from the solution with ions present in a solid matrix of the exchanger (synthetic zeolites or resins) with out any other significant chemical changes. A typical ion exchange resin sulphaoated polysterene, denoted by HR may be used. When a solution containing Ln^{3+} is passed down the column, the exchange of cations Ln^{3+} with protons of the resin takes place and an equilibrium is established as

$$Ln^{3+}\ (aq)\ +\ 3HR\ (S) \rightleftharpoons Ln(R)_3\ (S)\ +\ 3H^+ \qquad \text{---(1)}$$

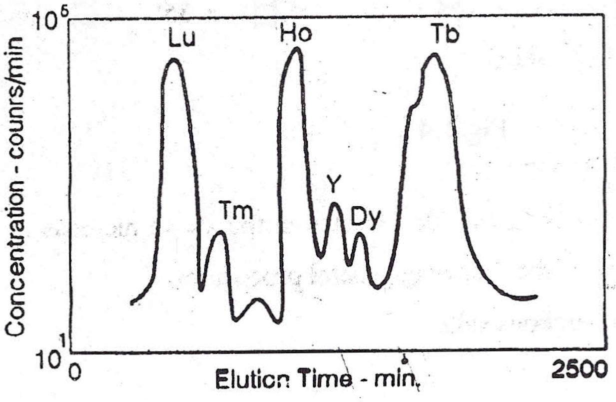
Two rate of ion exchange, is directly proportional to the concentration of the ions in the solution and charge on the ions in the solution; and is inversely proportional to the size of the hydrated ion which in run to the ionic size.

The degree of hydration increases from La^{3+} to Lu^{3+}, since the ionic size decreases from La^{3+} to Lu^{3+}

If the equimolar aqueous solution of Ln^{3+} ions passed through cation exchanger, the hydrated La^{3+} being smaller is exchanged first and the hydrated Lu^{3+} being the biggest exchanged last. After the lanthanide ions are adsorbed as different bands on the resin column, they are to be separated from the column for their individual separation. This releasing process is known as elution and the solution obtained after elution is called elute.

Russel and Tompkins used buffered citric acid solution for elution. The individual cations are released in the reverse order of the atomic number. The eluant is ammonium 2-hydroxy isobutyrate.

Fig.1.3



The other eluting solution is 0.1 to 0.2M EDTA adjusted to pH – 8 with ammonia when the elution solution percolates through the lanthanide band, the lanthanide ions pass into solution and are replaced in the resin by NH_4^+ from the complexing agent when the solution remove through the lower edge of the band, the displaced Ln^{3+} pass through first and exchange with H^+ on the resin below, but are then redissolved by the fresh NH^{4+} (aq) following up, so the whole band is gradually carried down the column. The stability of the complexes increases from La to Lu. Lanthanum ions displace Ce, which inturn displace Pr ions and so on, finally to displace and release Lu ions.

Powell, speeding et.al. used eluting solution of 5% ammonium citrate at pH 2.5-3.2 proved useful on microscale spread each lanthanide through a macro column (fig 1.4) in such a manner that extensive overlapping of the characterstic bell shaped electrical eluting curves (fig 1.5) could be prevented only by excessive increase in column length.

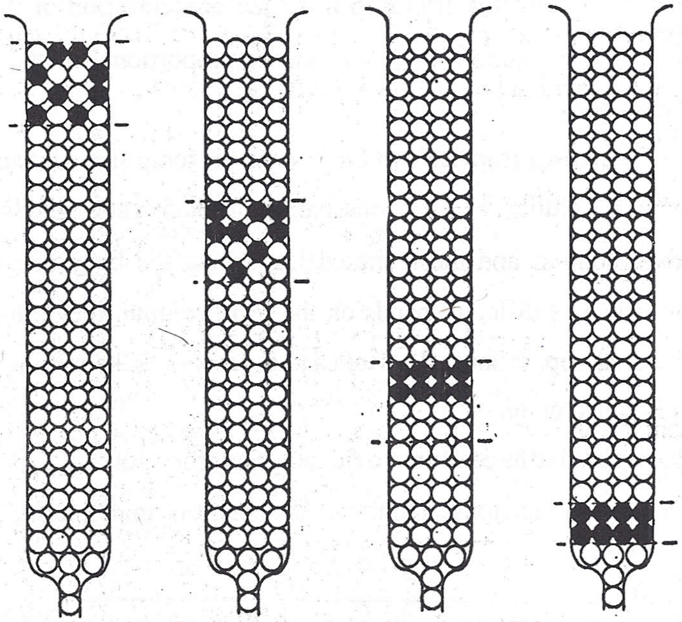


Fig 1.4

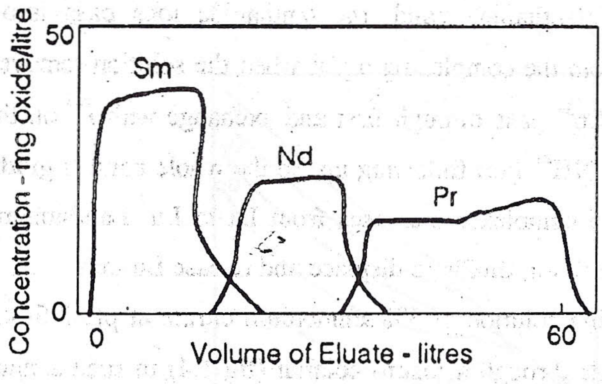


Fig 1.5

ii) Solvent extraction method.

In 1949, Warf observed that Ce^{4+} can be effectively separated from the tripositive lanthanide ions by extraction from aq. nitric acid solution by tri-n-butyl phosphate. This method is used on micro and macro scale method.

$$Ln^{3+}(aq) + 2NO_3^-(aq) + 3TBP(org) \leftrightharpoons Ln(NO_3)(TBP)_3(org) \qquad \text{---(2)}$$

The distribution between phases is expressed as

$$\lambda = \frac{C_{Ln(NO3)3\,(TBP)3\,(org)}}{C_{Ln3+}(aq).}$$

And for two lanthanides, the separation factor is

$$\alpha = \frac{\lambda^1}{\lambda}$$

Peppard found an average separation factor of $\alpha = 1.5$ for adjacent lanthanides in 15.8M nitric acid - 100% pure TBP systems.

The $\log_{10}\lambda$ is plotted against molar concentration of NO_3^- at constant concentration of TBP and a straight line with slope is obtained above 10M HNO_3 concs. (Fig.1.6). The graph also shows that extent of extraction increases with decreasing ionic radius.

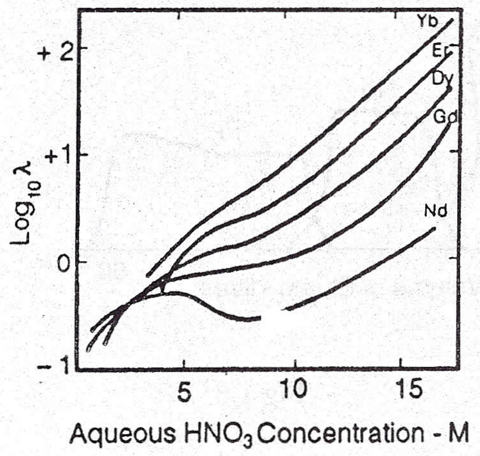


Fig.1.6

Another most effective organic solvent is di (2-ethyl hexyl) phosphoric acid. It gives the effective separation factor α=2.5 for adjacent lanthanides.

iii) Fractional crystallization.

Every anion found to form soluble salts with Ln^{3+}. Only those anions yielding truly isomorphous salts that are easy to crystallize, have reasonable and temperature dependent solubilities and possess measurable solubility difference as the Ln^{3+} ion changes are effective.

For eg. The more effective compounds are

- The double ammonium nitrates $Ln(NO_3)_3.2NH_4NO_3\ 4H_2O$ used for the removal La and separation of Pr from Nd.
- The bromates, $Ln(BrO_3)_3\ 9H_20$ and ethyl sulphates, $Ln(C_2H_5SO_4)_3\ 9H_2O$ for separation of members of yttrium group.

The procedure followed with double ammonium nitrates is –

The appropriate solution containing the mixed cations is evaporated until about half of the salts present will crystallize upon cooling to room temperature. The crystals are separated from the mother liquor. Each fraction is then recrystalised, the initial crystals by dissolving in water and evaporating until half the material deposits and the mother liquor by evaporating directly. Four fractions result. The mother liquor from the first crystals in this step is then combined with the second crystals and the operation repeated. In this way, the triangular scheme shown in fig 1.7 is developed, with the least soluble one (that of La^{3+}) concentrating at the head (crystal end) of the series, the moderately soluble one (Sm^{3+}) at the tail (solution end).

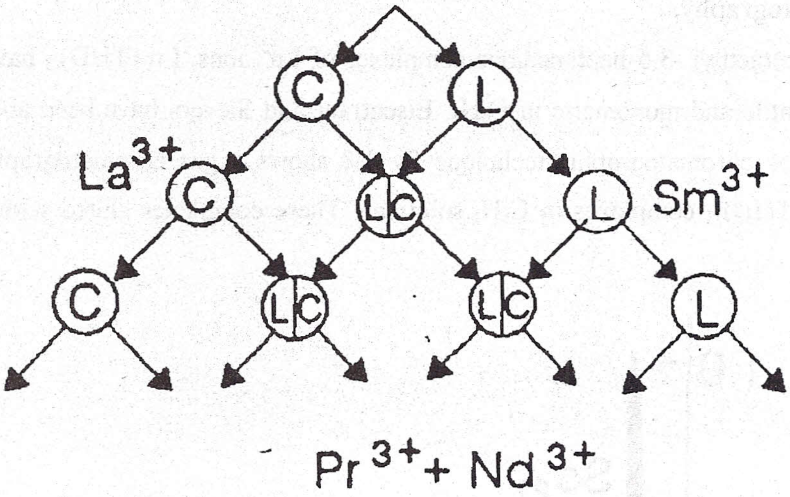


Fig.1.7

v) Fractional precipitation:

This is having little importance now. It depends fundamentally upon basicity differences. In the precipitation from homogeneous solution method for this method, the precipitation agents are developed in the Ln^{3+} ion solution. For eg. OH^- ions are produced by urea hydrolysis, oxalate ions are produced by hydrolysis of dimethyl oxalate. These basicity effects are achieved by adding a weak complexing agent or insufficient complexing agent (e.g. $EDTA^{4-}$ or NTA^{3-}) to tie up all the lanthanide ions before adding the precipitant. The least readily complexed cation is the most available for precipitation.

v) Paper chromatography:

Cerrai and Testa separated some rare earths by ascending paper chromatography using CRLI papers treated with 0.1 M dil (2-ethylhexyl) orthophosphoric acid (HDEHP). The R_F value increases with decreasing atomic number, Z. For a given element R_F values increases with the molarity of eluting acid, HCl and temperature, but decreases with concentration of HDEHP.

The R_F values for 1M HCl eluant are –

Ln3+	La	Ce	Pr	Sm	Eu	Gd	Dy	Er	Yb
R_F	0.92	0.91	0.90	0.76	0.64	0.51	0.12	0.06	0.03

Cerrai and Triulzi employed a mix of $3M HNO_3$ –80% CH_3OH as solvent on Whatman cellulose paper DE-20 (cellulose anion exchanger with amine groups) for separating La, Ce, Pr, Nd, Sm and Gd.

vi) Gas chromatography.

The 2, 2,6,6 – tetraethyl -3,5-heptanedione complexes of Ln^{3+} ions, Ln $(THD)_3$ have been found to be quite stable, volatile and monomeric in C_6H_6. Eisentraut and Sievers have been able to separate these complexes by gas chromatographic technique fig 1.8 shows a gas chromatographic separation of a mixture of Ln $(THD)_3$ complexes in C_6H_6 solution. These complexes eluted without decomposition.

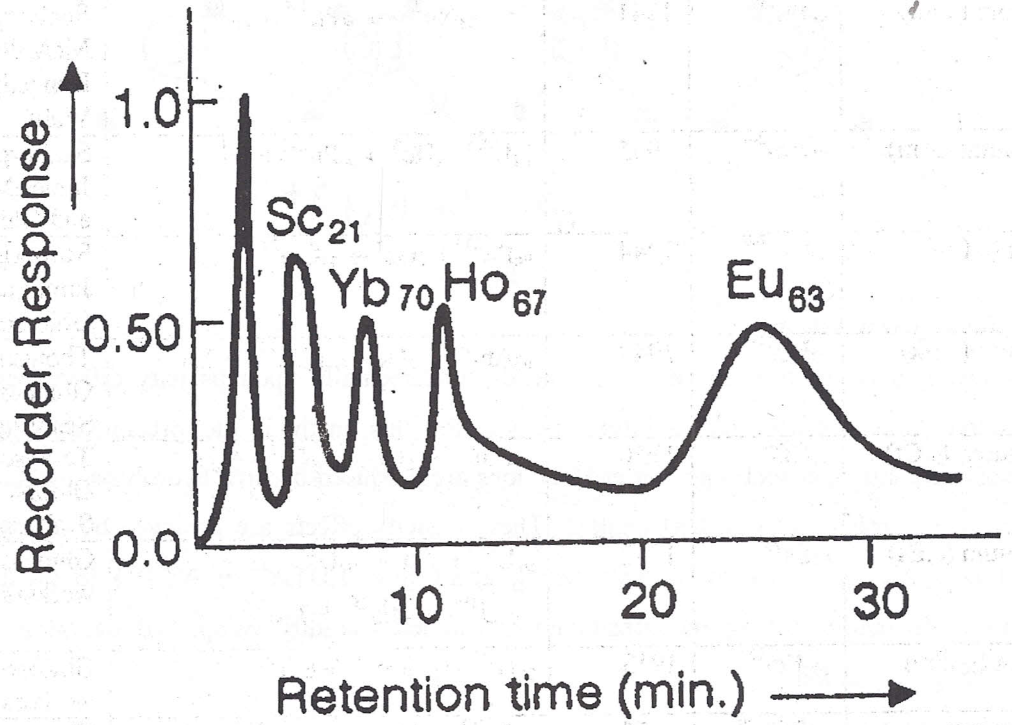


Fig 1.8

1.2.iv) Synthesis of transuranium elements-

Highest element which is naturally occurring uranium. After 1940 fourteen elements with At. No. from 93 to 106 were identified and synthesized by the transformation of naturally occurring elements by nuclear reactions. These manmade elements after uranium are collectively called as transuranium elements. The identification and synthesis is shown in table1.5.

Table 1.5

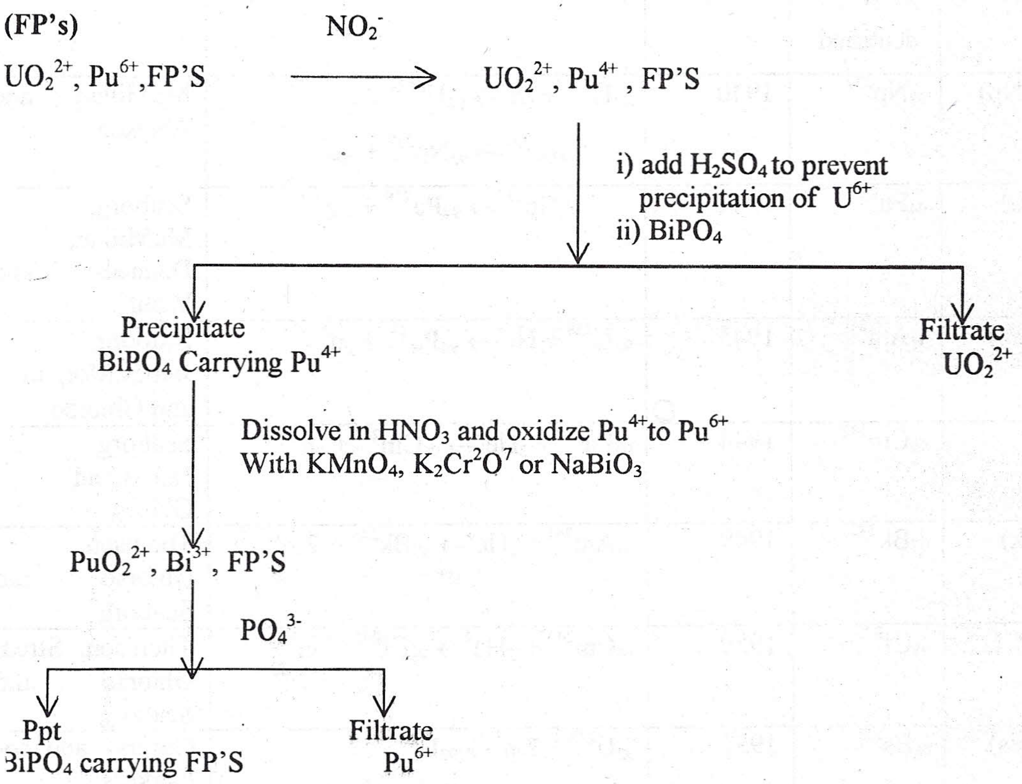
Trans-uranium Elements	First isotope dentified	Year	Source of synthesis	Discoverers
Neptunium ($_{93}$Np)	$_{93}Np^{239}$	1940	$_{92}U^{238} + {}_0n^1 \rightarrow {}_{92}U^{239}$ $_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}e^0$	McMillan and Abelson
Plutonium ($_{94}$Pu)	$_{94}Pu^{239}$	1941	$_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}e^0$	Seaborg, McMillan, Dennedy and Wahl
Americium($_{95}$Am)	$_{95}Am^{241}$	1945	$_{92}U^{238} + {}_2He^4 \rightarrow {}_{94}Pu^{241} + {}_0n^1$	Seaborg, James,Morgan and Ghiorso
Curium ($_{96}$Cm)	$_{96}Cm^{242}$	1944	$_{94}Pu^{239} + {}_2He^4 \rightarrow {}_{96}Cm^{242} + {}_0n^1$	Seaborg, James,and Ghiorso
Berkelium ($_{97}$Bk)	$_{97}Bk^{243}$	1949	$_{95}Am^{241} + {}_2He^4 \rightarrow {}_{97}Bk^{243} + 2_0n^1$	Thomson, Ghiorso and Seaborg
Californium ($_{98}$Cf)	$_{98}Cf^{245}$	1950	$_{96}Cm^{242} + {}_2He^4 \rightarrow {}_{98}Cf^{245} + {}_0n^1$	Thomson, Stred, Ghiorso and Seaborg
Einsteinium ($_{99}$Es)	$_{99}Es^{255}$	1952	$_{92}U^{238} + 7_0n^1 \rightarrow {}_{92}U^{255}$ $_{92}U^{255} \rightarrow {}_{99}Es^{255} + 7_{-1}e^0$	Ghiorso and co-workers
Fermium ($_{100}$Fm)	$_{100}Fm^{255}$	1953	$_{92}U^{255} \rightarrow {}_{100}Fm^{255} + 8_{-1}e^0$	Ghiorso and co-workers
Mendelevium ($_{101}$Md)	$_{101}Md^{256}$	1955	$_{99}Es^{253} + {}_2He^4 \rightarrow {}_{101}Md^{256} + {}_0n^1$	Ghiorso and co-workers
Nobelium ($_{102}$No)	$_{102}No^{252}$	1958	$_{96}Cm^{246} + {}_6C^{12} \rightarrow {}_{102}No^{252} + 6_0n^1$	Ghiorso Sikkelaw, Waton and Seaborg
Lawrencium ($_{103}$Lw)	$_{103}Lw^{254}$	1961	$_{98}Cf^{245} + {}_5B^{10} \rightarrow {}_{103}Lw^{254} + {}_0n^1$	Ghiorso and co-workers

1.2.v) Separation of actinide elements.

a) Precipitation method.

Tri and tetra– positive actinides are made to ppt as fluorides or phosphates from acidic solutions. Actinides in higher oxidation states either do not form a ppt or form complexes. This method is used for separation of actinide elements U-Am group. The summary of the process is shown in the flow sheet –3.

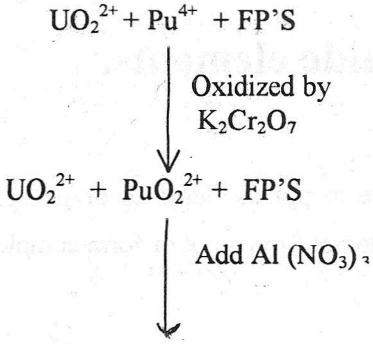
Flow sheet - 3 – $BiPO_4$ – Coupling method for the separation of Pu from U and fission products (FP's)

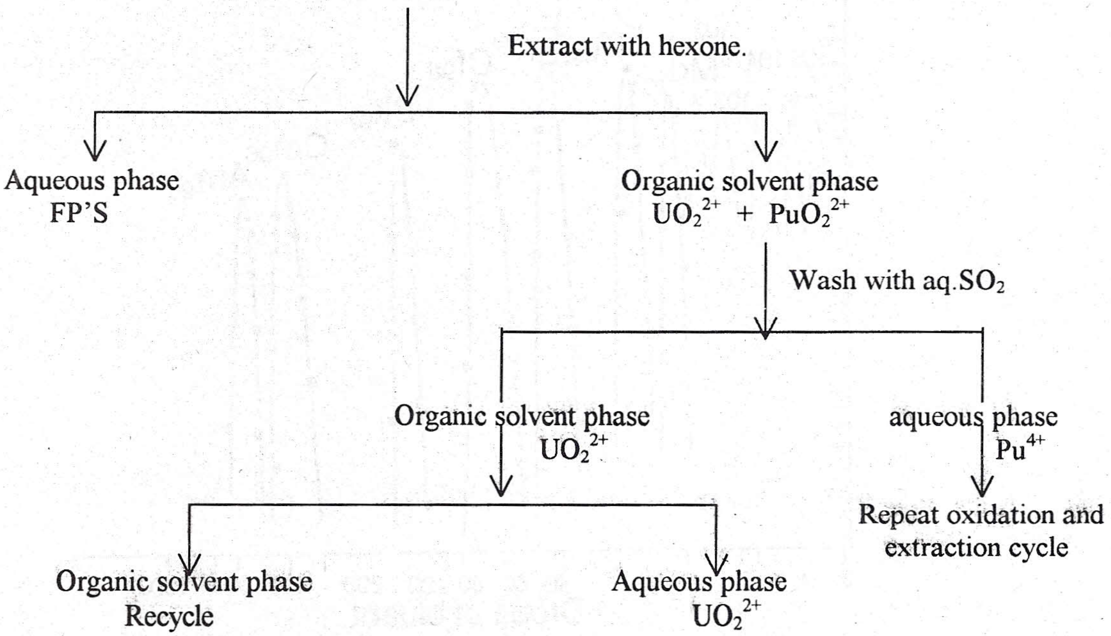


b) Solvent extraction method

This method is mainly used in the recovery of U and Pu from used up nuclear fuels and in based on the distribution of metal between the aqueous solution and an organic solvent. When treated with methyl isobutyl (hexone)- NP^{4+}, NP^{5+}, Pu^{6+} and U^{6+} are extracted and Pu^{4+} is not extracted. Other organic solvents can be used are diethyl ether and tri n-butyl phosphate (TBP) as 20% solution in kerosene. Solvent extraction of Pu and U by hexane and TBP has been shown in flow sheet no.4.

Flow sheet No.4 – Separation of Pu and U from fission products (FP'S) by solvent extraction process using hexone.





c) Ion – exchange technique:

This is best studied for separation of transamericium elements.

The method involves two steps-

i) Lanthanide – actinide separation – The actinides are a group can be separated from lanthanides by using a cation-exchange resin. Strong HCl finds use as the eluting agent. The actinide ions tend to form chloride complexes more readily and hence get eluted first.

ii) Separation of individual actinide elements – In general the actinide ions can be separated from each other by removing from the cation-exchanger by carrying out elution with ammonium citrate, lactate, α-hydroxy isobutyrate and EDTA. When the activity is made to plot against the no. of drops of eluant. Elution curves obtained is shown in Fig.1.9. Lw(103) is expected to leave the column first to be followed by No (102) and so on down the scale. Elution positions for Md(104) to Am(95) shown in the typical elution curves. Elusion curves exhibiting the elution position of actinide ions (An^{3+}) that are eluted from Dowex-50 ion-exchange resin with ammonia alpha-hydroxy isobutyrate is shown in Fig 1.9. The dotted elution curves reveal the predicted elution position of the then undiscovered elements with atomic numbers 102-103.

Fig 1.9

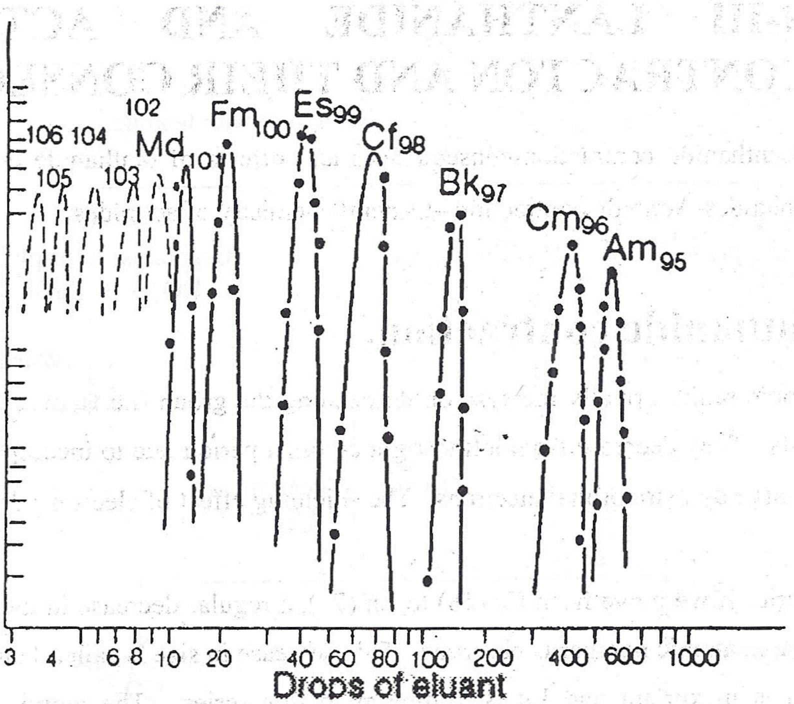


Fig 1.9 Elution curves exhibiting the elution Position of An^{3+} ions, which are eluted from Dowex-50 Ion-exchange resin with ammonia α-hydroxy isobutyrate.

1.2.vi) Model questions.

1. What are the minerals of lanthanides? Mention the main components of the mineral.
2. Write the cracking methods for the monazite.
3. Write any two methods for separation of lanthanides.
4. What the basic principles useful in the separation of lanthanides?
5. How the transuranium elements synthesized?
6. Write the method for the separation of actinides?
7. How the lanthanides can be separated from actinides?

1.2.vi) Recommended Books.

1.	F.A.Cotton and G.Wilkinson.	Advanced Inorganic Chemistry.
2.	J.E. Huhey	Inorganic Chemistry.
3.	J.D.Lee	Concise Inorganic Chemistry.
4.	G.F. Lipport	Modern Inorganic Chemistry.
5.	Gurdeep raj	Advanced Inorganic Chemistry

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LESSON-III LANTHANIDE AND ACTINIDE CONTRACTON AND THEIR CONSEQUENCES

Objectives – Lanthanide contraction-consequences and effects of lanthanide contraction-Chemical reaction of lanthanides-Actinide contraction –General chemistry of actinides.

1.3.i) Lanthanide contraction.

Covalent and ionic radii normally increase on descending the group (i.e from top to bottom), due to extra filled shells. They decrease from left to right across a period due to incomplete shielding of the extra nuclear charge by extra orbital electrons. The shielding effect of electrons decreases in the order s>p>d>f.

In lanthanide series if we move from Ce (58) to Ln (71), a regular decrease in the size of the atom or ion with increase in atomic number is observed. This decrease in size is called lanthanide contraction. The size of La is maximum and Lu is minimum in this series. The atomic and ionic radii of lanthanides are given in table 1.6.

Table 1.6

Elements	Atomic radii in pico meters (pm)	Ionic radii M^{3+} (in pm)
La	163	106
Ce	165	103
Pr	165	101
Nd	164	100
Pm	-	98
Sm	166	96
Eu	165	95
Gd	161	94
Tb	159	91
Ho	158	89
Er	157	88
Tm	156	87
Yb	170	86
La	156	85

The decrease in size, though continuous, is not regular. This is shown in fig 1.10.

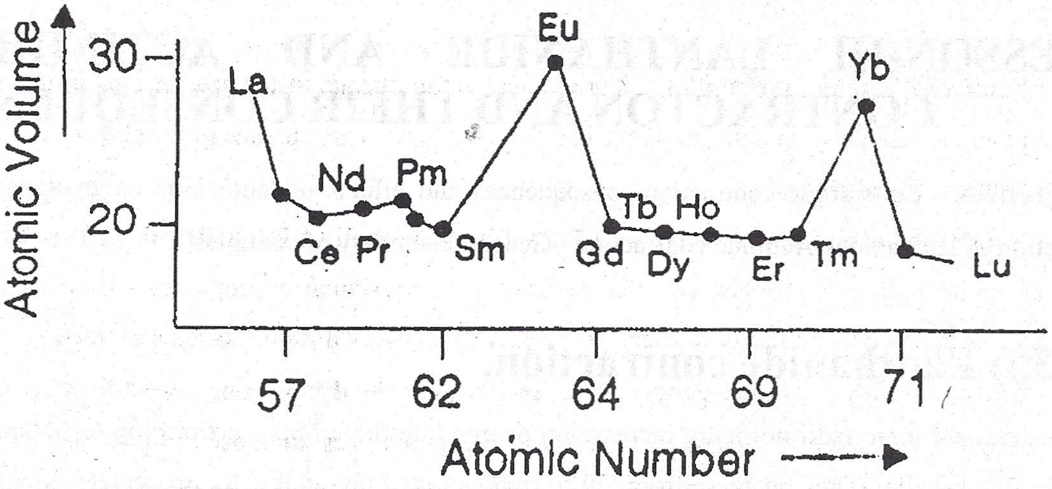

Fig 19. Atomic volume of lanthanide

We find from the figure that a general decrease in size (except Eu and Yb) takes place. This can be explained by the fact that lanthanide atoms contribute three electrons from $5d^1$ $6s^2$ towards the formation of metallic bond whereas Eu and Yb contribute only two electrons from $6s^2$ towards bond formation.

The reason for lanthanide contraction is due to imperfect shielding of one 4f-electron by another in the same sub-shell. On moving along the lanthanide series the no. of 4f electrons increases by one unit at each step and the imperfect shielding *zeff*, increases causing a contraction of electron cloud of the 4f sub shell. Ionic radii change from 106 to 85. The contraction in size from one element to another is fairly small, however the addition effect over 14 elements (Ce to La) is about 21pm.

1.3.ii) Consequences and effects of lanthanide contraction.

The lanthanide contraction plays an important role in chemistry of lanthanides. The important consequences of lanthanide contraction are-

a) there is steady decrease in ionic size.

b) The hardness, M.P and B.P increase from Ce to Lu because of the attraction between atoms increases as the size decreases.

c) There is slight increase in electro negativity of trivalent ion.

d) The potential values (E_0) for $M^{3+} + 3e \rightarrow M$ increase regularly from lanthanum –2.52 V to lutetium 2.25 V. So there is a regular decrease in their tendency to act as reducing agents.

e) Since charge is same and size is small, their chemical proportions are very similar.

The effects of lanthanide contraction are-

a) Similarity among lanthanides – there is very small change in the size of ions in lanthanide series and there is no change in outer most shell so there is a close resemblance in the chemical properties of lanthanides.

b) Similarity in properties of Ho and Dy – The ionic radii of Dy is 91 pm , Ho is 89 and that of yttrium is 90pm. Due to this, the three elements are very similar in properties. They occur together in minerals and due to similarity in chemical properties it is very difficult to separate them.

c) Close resemblance in the properties of second and third transition series-Because of lanthanide contraction the size of the elements that follow the lanthanides are close to those of the previous row. It is responsible for the existence three pairs of elements which are having the similar properties.

	a) Zr and Hf,	b) Nb – Ta,	c) Mo - W etc.
Covalent radii	145 144	134 - 134	129 - 130

The third transition series have virtually the same atomic and ionic radii as the corresponding elements just above them in their respective subgroups.

The covalent radii (in pm) values of some elements reflecting the effect of lanthanide contraction on the atomic radii of the third transition series elements are given in table 1.7

Table –1.7

III A		IVA	VA	VIA	VIIA		VIII		IB
Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu
164		145	137	125	137	124	125	125	128
Y		Zr	Nb	Mo	Te	Ru	Rh	Pd	Ag
180		159	143	136	132	133	135	138	144
La	Ce-La	Hf	Ta	W	Re	Os	Ir	Pt	Au
188	182-173	156	143	137	137	134	136	139	144

If we go down in the period, the atomic size increases but if we compare second and third transition elements, the size is not increased and is almost same. This is because, the third transition elements comes after lanthanides. Due to the effect of lanthanide contraction, the size of the third transition elements is not increase and is almost same as that of second transition elements. If we observe the above table, there is a difference in sizes is more between first and second transition elements but the difference is less between second and third transition elements.

The decrease in third transition elements which follow lanthanides is due to lanthanide contraction, that is why the pairs Zr (second transition element) and Hf (third transition element) or Nb and Ta, Mo-W etc have similar properties.

d) Basicity differences- As the atomic number increases, there is a decrease in basic strength of oxides and hydroxides. So $La(OH)_3$ is most basic and $Lu(OH)_3$ is least basic. This is also due to lanthanide contraction. The successive decrease in size of lanthanide cations increases successively the covalent character (decreases the ionic character) between the lanthanide ion and hydroxide ion (Fajan's rules) there by reducing the basic character of lanthanide hydroxides. Thus basicity of Ln^{3+} ions may be expected to decrease in the order-

$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Ea^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$.

The differences in basicity are effected in

1. Hydrolysis of ion – More basic the ions, hydrolyse with difficulty and less basic ions hydrolyse more readily. That is why there is a slight increase in degree of hydrolysis in solution is observed from La^{3+} and Lu^{3+}.
2. Solubility of salts – The precipitation of hydroxides takes place at progressively decreasing pH values from La^{3+} to Lu^{3+}. For e. La^{3+} at pH 6.82, Lu^{3+} at pH 6.30.
3. Thermal decomposition of oxysalts – The thermal stability of trinitrate salts decreases as we move along the series.
4. Formation of complexes – The tendency to form complex ions increases in moving along the series.
5. Occurrence of yttrium (a transition element) with heavier lanthanides – As the size of the Y^{3+} ion (90pm) has been comparable to the heavier lanthanide ions viz. Tb^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+}, the former is found with the later in natural minerals. Because the crystal structure, solubility and chemical properties of the yttrium are close to heavier lanthanides, the heavier lanthanides are commonly termed as yttrium earths.

1.3.iii) Physical Properties

Lanthanides show some variations in physical properties

a) Ionization energy – First ionization energy is about 588 KJ mol^{-1} and second ionization energy is about 1155 KJ mol^{-1}. These are closely comparable with ionization energies of the alkaline earth metals particularly of calcium.

b) Electronegative values – These range between 1.0-1.15 and are of same order as those of s-block elements. So lanthanides form ionic compounds.

c) Metallic radii – The metallic radii are in the same range as those of s-block (174pm). It suggests that they are fairly large atoms. The large interatomic distance in case of Eu and Yb are because of differences in crystal structure. Eu and Yb has body-centered cubic (bcc) and others have hexagonal close packed (hcp) type crystal structure.

d) Physical constants – Densities and M.P of lanthanides are given in table 1.8.

Table 1.8

Element	Density g.cm^{-3}	M.P. (°C)
La	6.17	920
Ce	6.77	795
Pr	6.78	919
Nd	7.00	1020
Pm	-	1080
Sm	7.54	1070
Eu	5.26	826
Gd	7.9	1306
Tb	8.27	1356
Dy	8.54	1500
Ho	8.8	1460
Er	9.05	1497
Tm	9.33	1545
Yb	6.98	824
Lu	9.84	1652

The density and M.P. changes gradually except in the case of Ce, Eu and Yb. The lower values of Eu and Yb may be due to the fact that Yb form +2 ions which results in slightly weakly metallic bonds thus M.P and B.P are lower.

1.3.iv) Chemical reactions of lanthanides.

a) Lanthanides form binary compounds. Form oxides, M_2O_3 , which resemble the Ca-Ba group oxides. M_2O_3 absorbs CO_2 and H_2O from the air to form carbonates and hydroxides.

b) Lanthanides reacts with hydrofluoric acid or fluoride ions and precipitates as MF_3 even in 3M HNO_3.

$$M^{3+} + 3F^- \rightarrow MF_3 \downarrow \qquad \text{---(3)}$$

This is the characteristic test for lanthanide ions. Heavier lanthanides are slightly soluble in excess of HF owing to formation of complex.

C Metal chlorides are formed on heating metal oxides with NH_4Cl.

$$M_2O_3 + 6NH_4Cl \xrightarrow{\sim 300^\circ C} 2MCl_3 + 3H_2O + 6NH_3 \qquad \text{---(4)}$$

d) Semiconducting sulphides can be formed by the reaction of

$$2MCl_3 + 3H_2S \xrightarrow{1110^0C} M_2S_3 + 6HCl \qquad ---(5)$$

e) Double salts are more common.

For eg. $2M(NO_3)_3 .3Mg(NO_3)_2.24H_2O$.

$M(NO_3)_3.2NH_4NO_3.4H_2O$.

$M(SO_4)_3.3Na_2SO_4.12H_2O$.

f) Lanthanides on reaction with ammonium oxalate in neutral solution gives normal oxalates but heavier lanthanides gives mixtures.

g) the metals react with H_2 on heating up to 300-400^{0}C and form solid hydrides of formula LnH_2.

h) Lanthanide ions reacts with many ligands to form complexes. Some lanthanide complexes listed in table 1.9

Table 1.9

Some lanthanide complexes.

Coordination No.	Complex	Shape
4	$[Lu\ (2,6\text{-dimethyl phenyl})_4]^-$	Tetrahedral
6	$[Ce\ Cl_6]^{3-}$	Octahedral
7	$[Y\ (\text{acetyl acetone})_3\ (H_2O)$	Monocapped tri gonal prism
8	$[La\ (\text{acetyl acetone})_3\ (H_20)_2]$	Square antiprism.
8	$[Ce\ (\text{acetyl acetone})_4]$	Square antiprism
9	$[Nd\ (H_2O)_9]^{3+}$	Tricapped trigonal prism
10	$[Ce\ (NO_3)_4 (PH_3PO)_2]$	Each $NO_3$is bidendate
12	$[Ce\ (NO_3)_6]^{2-}$	Icosahedral

1.The aqua complexes –

$$[M\ (H_2O)n]^{3+} + H_2O \longrightarrow [M\ (OH)(H_2O)_{n-1}]^{2+} + H_3O^+ \qquad ---(6)$$

$$3Ce^{3+} + 5H_2O \longrightarrow [Ce_3\ (OH)_5]^{4+} + 5H^+ \qquad ---(7)$$

2. Halogen complexes -

MX_6^{3-} are formed in non-aqueous media such as ethanol or acetonitrile

$$NdCl_3 + 2Al_2Cl_6 \longrightarrow Nd\ Al_4Cl_{15} \qquad ---(8)$$

3. Sulphide complexes-

Dithiocarbonates (dtc) made from

$$MBr_3 + NaS_2CNR_2 \xrightarrow{\text{eather}} M\ (dtc)_3 \qquad ---(9)$$

4. Organic complexes-

Examples are- $M(C_5H_5)_3$, $M(C_5H_5)_3\ CNC_6H_{11}$. $K[M(COT)_2]$ where COT is cycloocta tetraemide, $M(C_6H_5)_3$

i). At elevated temperature the metals reacts with N, P, Al, Sb and Bi giving LnN etc and later hydrolyzed by water as

$$LnN + 3H_2O \longrightarrow Ln(OH)_3 + NH_3 \qquad ---(10)$$

On arc melting the metals with carbon in an inert atmosphere form carbides, LnC_2 and $Ln_4(C_2)_3$. There are more reactive

$$2LnC_2 + 6H_2O \longrightarrow 2Ln(OH)_3 + C_2H_2 + H_2 \qquad ---(11)$$

$$C_2H_2 + H_2 \longrightarrow C_2H_4 \xrightarrow{H_2} C_2H_6 \qquad ---(12)$$

1.3.v) Actinide contraction.

As in lanthanides, in actinides, the atomic radii and ionic radii decreases with increasing atomic number. This decrease is called actinide contraction and is ascribed to the addition of successive electrons to an inner f shell (i.e. 5f shell), so that imperfect screening of the increasing nuclear charge by the addition of 5f electrons causes a contraction of the outer or valence orbital. In table 1.9, atomic and ionic radii (crystal structure date form the basic) of An^{3+} and An^{4+} ions are given.

Table 1-10

Atomic and ionic (or crystal) radii of actinides.

Element	Atomic No.	Atomic radius in picometers (pm)	An^{3+} ion (pm)	An^{4+} (pm)
Ac	89	188	111	99
Th	90	180	108	96
Pa	91	161	105	93
U	92	138	103	92
Np	93	130	101	92
Pu	94	151	100	90
Am	95	173	99	89
Cm	96	-	98	88

The jumps in contraction between the consecutive elements in the actinides have been found to be greater than in the lanthanides. The greater contraction is attributed to the lower shielding of 5f –

electrons which are therefore, pulled more strongly by the nucleus. The Am^{3+} ion has always been larger than analogous Ln^{3+} ion which is shown in fig. 1.11. which

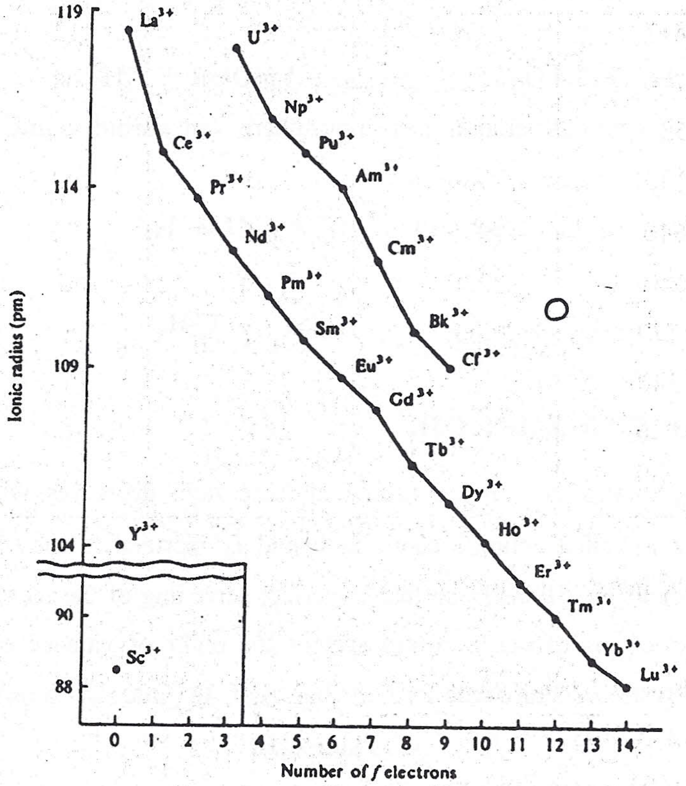

Fig. 1.10. Ionic radii of Ln^{3+} and An^{3+} ions.

The readily detectable discontinuity at Gd^{3+} ion is not having a parallel at the Cm^{3+} ion but a continuing divergence exists in size among the An^{3+} ions as the nuclear charge increases.

1.3.vi) General properties of Actinides.

The elements are all silvery white. The M.Ps are moderately high, but are considerably lower than those for the transition metals. The size of the ions decreases regularly along the series, because of the extra charge on the nucleus is poorly screened by the f electrons. The ionic radii of M^{3+} of lanthanides and actinides ions are very similar in size. Hence their chemical properties are alike. The actinides have much higher densities and a much grater tendency to form complexes. Some of the properties of actinides are given in table 1.11

Table 1.11

Properties of actinides.

Element	M.P ^0C	B.P ^0C	Density $g.cm^{-3}$	Radius M^{3+} (pm)	Radius M^{4+} (pm)
Ac	817	2470	-	112	-
Th	1750	4850	11.8	108	94
Pa	1552	4227	15.4	104	90
U	1130	3930	19.1	103	89
NP	640	5235	20.5	101	87
Pu	640	3230	19.9	100	86
Am	1170	2600	13.7	98	85
Cm	1340	-	13.5	97	85
Bk	986	-	14.8	96	83
Cf	900	-	-	95	82

The actinides are reactive metals. They react with

i) Hot water.

ii) Tarnish in air and forms an oxide coating.

iii) HCl, conc, HNO_3 passivates.

iv) Do not react with NaOH because they are basic.

v) Oxygen, halogen.

vi) Hydrogen and form hydrides which are non-stoichiometric and have ideal formula MH_2 and MH_3.

The metals are obtained by electrolysis of fused salts or by reducing the halides with Ca at high temperature.

They form complexes with organic ligands. Examples are $(C_5H_5)_3UCl$, $(C_5H_5)_3Am$, $(C_5H_5)_2Pu$. (Sandwich structure). High coordination number complexes are formed by thorium. The examples are

1. $K_4[Th(oxalate)_4].4H_2O$ with C.No.8 (square antiprism).
2. $(NH_4)_4[ThF_8]$ with C..No. 9 (Tricapped trigonal prism ThF9).
3. Mg $[Th(NO_3)_6]$ with C.NO. 12 (Icosoheral. NO^{3-} bidentate).

The isotopes of the actinides are –

^{232}Th, ^{238}U, ^{237}Np, ^{239}Pu, ^{231}Pa, ^{238}Pu, ^{242}Pu, ^{241}Am, ^{243}Am, ^{244}Cm, ^{244}Pu, ^{249}Bk, ^{242}Cm, ^{252}Cf, ^{253}Es, ^{254}Es, ^{257}Fm.

1.3.vii) Model questions.

1. What is lanthanide contraction? explain.
2. What is the effect of lanthanide contraction on second and third transition elements?
3. Discuss about the basicity differences among lanthanides.
4. Write the chemical reactions of lanthanides?
5. What is an actinide contraction? explain.
6. Discuss about general properties of actinides?
7. Compare the decrease in atomic and ionic radii of lanthanides with actinide? Ascertain reasons.

Recommended Books.

1. F.A.Cotton and G.Wilkinson.	Advanced Inorganic Chemistry.
2. J.E. Huhey	Inorganic Chemistry.
3. J.D.Lee	Concise Inorganic Chemistry.
4. G.F. Lipport	Modern Inorganic Chemistry.
5. Gurdeep raj	Advanced Inorganic Chemistry.

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LESSON - IV MAGNETIC AND SPECTRAL PROPERTIES OF LANTHANIDES AND ACTINIDES, AND THE USES OF THEIR COMPOUNDS.

Objectives – Magnetic and spectral properties of lanthanides – Magnetic and spectral properties of actinides – comparison of lanthanides and actinides – uses of the lanthanides and actinide compounds.

1.4.i). Color and spectra of lanthanides.

The trivalent lanthanide ions are colored both in the solid state and aqueous solution. The color depends on number of unpaired 4f electrons. Elements with (n)f electrons often have a similar color to those of (14-n)f electrons. For e.g. Pr^{3+} having in 4f two electrons green in color, similarly Tm^{3+} having in (14-2)f i.e.12 electrons pale green in color. The color of Ln^{3+} ions are given in table 1.12.

Table 1.12.

Colors of Ln^{3+} ions.

Ln^{3+} ion	No. of 4f electrons	Color	Ln^{3+} ion	No. of 4f electrons	Color
La^{3+}	0	Colorless	Ln^{3+}	14	Colorless
Ce^{3+}	1	Colorless	Yb^{3+}	13	Colorless
Pr^{3+}	2	Green	Tm^{3+}	12	Pale green
Nd^{3+}	3	Lilac	Er^{3+}	11	Pink
Pm^{3+}	4	Pink	Ho^{3+}	10	Pale yellow
Sm^{3+}	5	Yellow	Dy^{3+}	9	Yellow
Eu^{3+}	6	Pale pink	TB^{3+}	8	Pale pink
Gd^{3+}	7	Colorless	GD^{3+}	7	Colorless

The elements in the other valency states i.e., Ln^{4+}, Ln^{2+}, do not all have colors similar to their isoelectronic Ln^{+3} counterparts. For eg. Ce^{4+} with $4f^0$ is orange red while the counterpart La^{3+} ($4f^0$) is colorless. The colors are given in table 1.13.

Table 1.13

Colors of Ln^{4+} and Ln^{2+} and their isoelectronic Ln^{3+} counterparts.

Ion	Color	Electronic Configuration	Isoelectronic Ln^{+3} ion	Color
Ce^{4+}	Orange-red	$4f^0$	La^{3+}	Colorless
Sm^{2+}	Blood-red	$4f^6$	Eu^{3+}	Pale pink
Eu^{2+}	Pale greenish yellow	$4f^7$	Gd^{3+}	Colorless
Yb^{2+}	yellow	$4f^{14}$	Lu^{3+}	Colorless

Color arise because light of a particular λ is absorbed in the visible region. In the lanthanides the spin-orbit coupling is more important than crystal field splitting (which is important in transition elements). Except Lu^{3+} (which has full f shell), all lanthanide ions show absorption in the visible or near U.V region.

The spectra arise due to –

a) from f-f transitions

b) these are Laporte forbidden since $\Delta l = 0$.

c) the colors are pale because they depend on relaxation of the rule.

d) the f orbitals are deep inside the atom and shielded well from nature and number of ligands.

e) the position of absorption band does not change by different ligands.

f) vibration of ligands changes the external fields, which only splits the various spectroscopic states by about $100 cm^{-1}$, so the absorption bands are unusually sharp. So in lanthanides the sharp absorption bands are obtained.

The differences in spectra of lanthanide ions and transition metals are given in table 1.14.

Table 1.14

Lanthanides	Transition metals
1. Spectra due to f-f transition	Spectra due to d-d transition
2. Laporte forbidden	Laporte forbidden but some d-p mixing.
3. Pale	Intense.
4. Does not depend on nature and number of ligands.	Depends on the ligands.
5. Does not depend on crystal field splitting.	Depend on crystal field splitting.
6. Shape or narrow peaks.	Broader peaks.

Ce^{3+} and Yb^{3+} are colorless because they do not absorb in the visible region. They show exceptionally strong absorption in the U.V region, because of transition of electron from 4f to 5d.

The reason is 1) $\Delta l = 1$ 2) the promotion of electron from 4f to 5d is easlier.

Charge transfer spectra are possible in some lanthanide ions. This is probable if the metal is in high oxidation state or the ligand has reducing properties. Strong yellow color of Ce^{4+} solution and blood red color of Sm^{2+} solution is due to charge transfer spectra.

1.4.ii). Magnetic properties of lanthanides.

La^{3+} and Ce^{4+} $(4f^0)$ and Lu^{3+} $(4f^{14})$ have no unpaired electrons are diamagnetic. All other Ln^{3+} ions are paramagnetic.

The magnetic movement using spin and orbital momentum can be calculated from the equation-

$$\mu_{(S+L)} = \sqrt{4S(S+1)+L(L+1)} \text{ B.M} \qquad \text{---(13)}$$

Where S= resultant spin Q.NO. of atom

L= resultant orbital Q.NO. of atom

Magnetic moment due to spin only we can calculate using

$$\mu_S = \sqrt{4S(S+1)} \qquad \text{---(14)}$$

or

$$\mu_S = \sqrt{n(n+2)} \quad \text{where n=No. of unpaired electrons} \qquad \text{---(15)}$$

For eg. For $La^{3+}(f^0)$ $\mu_S = \sqrt{0(0+2)} = 0$ ---(16)

$$Gd^{3+}\,(f^7)\ \mu_S = \sqrt{7\,(7+2)} = 7.9 \text{ B.M.} \qquad \text{---(17)}$$

For other lanthanides this simple calculation is not sufficient since 4f electrons are shielded from external fields by the overlapping 5s and 5p electrons. So the μ can be calculated from the unpaired electron spin and orbital motion. In the lanthanides in contrast to transition metal ions, there is L-S coupling. Then

$$\mu = g\sqrt{J(J+1)} \qquad \text{---(18)}$$

$$\text{Where } g = 3/2 + \frac{S\,(S+1) - L\,(L+1)}{2J\,(J+1)} \qquad \text{---(19)}$$

the magnetic movement calculated using spin only (eq.15) and using spin-orbital coupling (eq.18) for lanthanides is depicted in Fig.1.12.

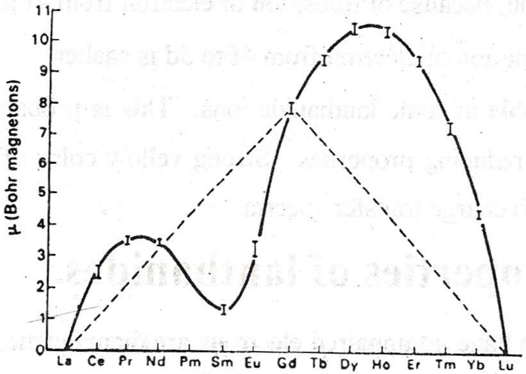

Fig.1.12

μ values of Ln^{3+} at 300^0C 1. Spin only values by dashed line 2. L+S as solid line.

For most of the lanthanides there is excellent agreement between the calculated values using μ_{S+L} and experimental values measured at 300^0K. The agreement for Eu^{3+} and Sm^{3+} are poor. The reason is that with Eu^{3+}, the spin-orbit coupling contrast is only 300 cm^{-1} (i.e the energy difference of ground state and next state is small). Thus the energy of thermal motion is sufficient to promote some electrons and partially populate the higher state. So μ is not solely determined by ground state configuration. The unusual shape is of the curve is less than half fill, J=L-S and when half-fill or more J=L+S.T

The magnetic movements of Ln^{3+} ions calculated and experimental values are given in table 1.15.

Table 1.15

Element		Electronic configuration M^{3+}	Magnetic movement μ	
			Cal	Fe pH
Lanthanum	La	[Xe] 4f0	0	0
Cerium	Ce	[Xe] 4f1	2.54	2.3 – 2.5
Praseodymium	Pr	[Xe] 4f2	3.58	3.4 – 3.6
Neodymium	Nd	[Xe] 4f3	3.62	3.5 – 3.6
Promethium	Pm	[Xe] 4f4	2.68	2.7
Samarium	Sm	[Xe] 4f5	0.84	1.5 – 1.6
Europium	Eu	[Xe] 4f6	0	3.4 – 3.6
Gadolinium	Gd	[Xe] 4f7	7.94	7.8 – 8.0
Terbium	Tb	[Xe] 4f8	9.72	9.4 – 9.6
Dysprosium	Dy	[Xe] 4f9	10.63	10.4 – 10.5
Holmium	Ho	[Xe] 4f10	10.60	10.3 – 10.5
Erbium	Er	[Xe] 4f11	9.57	9.4 – 9.6
Thallium	Tm	[Xe] 4f12	7.63	7.1 – 7.4
Ytterbium	Yb	[Xe] 4f13	4.5	4.4 – 4.9
Lutetium	Lu	[Xe] 4f14	0	0

1.4.iii). Color and spectra of actinide ions.

The colors of actinide ions, An^{3+}, An^{4+} AnO^{2+} and AnO_2^{2+}, are given in table 1.16. An^{3+} ions are roughly having comparable colors with the Ln^{3+} ions for the same no. of f electrons. For eg. U^{3+} ($5f^3$) and Nd^{3+} ($4f^3$) ions reddish in color. Similarly Cm^{3+} ($5f^7$) and Gd^{3+} ($5f^7$) are colorless.

Table 1.16

Colors of actinide ions and their wavelength in nm. of absorption bands.

Element	Am^{3+}	An^{4+}	AnO_2^{+}	AnO_2^{2+}
Ac	Colorless $5f^0$	-	-	-
Th	-	Colorless, ($5f^0$)	-	-
Pa	-	Colorless 224, 255, 276	Colorless	-
U	red $5f^3$ 520, 880,900	Green $5f^2$ 550,650.	-	Yellow 400,411,425.
Np	Blue or purple, $5f^4$ 552, 661, 788	Yellow green, $5f^3$ 504, 743, 825	Green	Pink to red 476, 557.
Pu	Blue or violet, $5f^4$ 560, 600, 603	Turn to orange brown, $5f^4$ 470, 655, 815.	Reddish purple	Yellow to pink orange 834, 953, 983.
Am	Pink, $5f^6$ 503,820.	Rose, $5f^7$	Yellow 513.	Sun colored 666.
Gm	Colorless, $5f^7$ 237, 268.	-	-	-

The absorption spectra of actinide ions, in aqueous solution and in crystals, are having sharp or narrow bands, in the visible, near U.V and I.R regions of spectrum. The absorption spectra is obtained due to f-f transitions (in 5f shell). The absorption bands in the case of actinides are about ten times sharper than lanthanides. Charge transfer spectra also obtained in actinides and the bands are more intense because of lower energy involved in transitions. Intensity increases with the increase of overlap of 5f orbitals with ligand orbitals.

1.4.iv). Magnetic properties of actinides ions

In actinides, Pu^{3+} and Am^{3+} ions have been found to exhibit the analogous behavior as that for Sm^{3+} Eu^{3+} ions in lanthanide series. The magnetic moments values calculated from L-S coupling are higher than experimentally observed. This may be due to in adequacy of more suitable ligand field effects which involved 5f orbitals to a greater extent than the 4f orbitals which are involved in bonding in the lanthanide complexes. The 5f electrons of the actinide ions have been less effectively screened from the crystal field. The orbital magnetic momentum is quenched. The molar magnetic susceptibility can be calculated from the eq. 20.

$$x_M = \frac{N^{g2}B^2J(J+1)}{3KT} + N\alpha \qquad \text{---(20)}$$

Where N = Avagadro's number

g = lande splitting factor (eq. 18)

B = Bohr magneton $= \frac{eh}{2\pi\ mc} = 9.27\ x10^{-21}$ erg/gauses

J = Total angular momentum of atom = (L+S)

K = Boltzman constant = $1.3805\ x\ 10^{-16}$ erg deg^{-1}

T = Absolute temperature

α = Small, temp. independent term due to second order zeeman effect

There are remarkable similarities in the molar magnetic susceptibilities of actinide and lanthanide ions. The comparison of magnetic moments of actinide and lanthanide ions in shown in fig 1.13

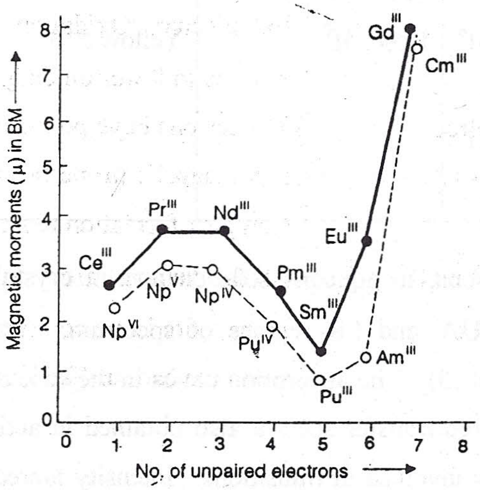

Fig 1.13 / Magnetic susceptibilities of actinide and lanthanide ions. Dashed line – actinides and solid line – lanthanides.

1.4.v). Comparison of Lanthanides and Actinides

Lanthanides and actinides are belongs to inner transition elements. In both f electrons are filled by electrons orbitals. Both are having some similarities and some differences.

The similarities of both are –

a. show +3 oxidation state.

b. f-orbitals of (n-2) shell are progressively filled up with electrons.

c. a contraction in atomic size is observed with increase in atomic number.

d. sharp absorption spectra bands obtained due to f-f transitions.

e. electro negativity is low.

f. reactive.

g. nitrate, perchlorate and sulphate salts are soluble.

h. carbonates and hydroxides are in soluble.

The differences between lanthanide and actinide series are shown in table 1.17.

Table 1.17.

Lanthanides	Actinides
1. Chemical properties of all of the elements are similar. This is due to large energy difference is 4f and 5d sublevel.	Considerable variation is there. This is due to very small energy difference between 5f and 6d sub-level.
2. Have high binding energy	Have small binding energy.
3. Exhibit max. oxidation state is +4	Exhibit max. Oxidation state upto +7(+4, +5, +6, +7) due to lower binding energies.
4. 4f electrons have better shielding effect	5f electrons have poor shielding effect.
5. Paramagnetic properties can be easily explained	Paramagnetic properties explanation is difficult.
6. Complex formation tendency is not high	Complex formation tendency is very high.
7. Except Pm, these are not radioactive.	All the elements are radioactive.
8. Form less basic compounds	Form more basic compounds.
9. Oxycations are not formed	Form oxycations like UO_2^{2+}, U^{8+}, NPO_2^{2+}; PuO_2^{2+}

1.4.vi). Uses of Lanthanide compounds.

a) Nuclear applications

1. Some of the lanthanides are used in atomic reactors to control the rate of fission. Gadolinium, (Gd 157), has large neutron stopping capacity. Sm^{140}, Eu^{151}, Dy^{164} also can be used next.
2. Lanthanide isotopes are used in some atomic batteries as gamma – ray or x-ray sources, as radioactive materials for treatment of cancer in traces studies.

b) Metallurgical applications.

Some of the metals and alloys of lanthanide elements find important metallurgical applications as reducing agents.

1. Misch metals is having strong reducing property. It is a very good scavenger for oxygen and sulphur in several metallurgical operations. The composition is – Ce – 45 to 50%, La-22 to 25%, Nd-18%, Pr 5% Sm 1% and other lanthanides is small quantities.
2. Magnesium alloys with misch metal 3% and Zr 1% possesses high strengths and resistance and are useful in jet engines.
3. Misch metals increase the resistance of nickel alloys.

c) Ceramic applications.

d) The lanthanide compounds are useful. The CeO_2 is used for grinding and polishing optical glass. The La_2O_3 is used in camera lenses to reduce chromatic abrration. Lanthanide oxides are dissolved in glass to impart beautiful colors to glass windows. CeO is used in crooks glass. Pro, NdO also used for coloring glass in the production of standard light filters.

d) Catalytic applications.

The oxides of lanthanides are used in hydrogenation, dehydrogenation and oxidation of various organic compounds, for eg, cerium phosphate is used in petroleum cracking.

e) Magnetic and electronic application.

The ferromagnetic garnets of $3Ln_2O_3$ $5Fe_2O_3$ types are used in microwave devices.

f) Medicinal applications. Some rare-earth compounds are used in medicines for treatment of diseases like eczema, leprosy etc.

g) Low temperature applications.

$Gd_2(SO_4)_3 .7H_2O$ is used to produce very low temperature.

h) Rare earth fluoride compounds are used to produce cored carbon pencils used in projectors in move theatre.

1.4.vii) Uses of Actinide compounds.

a). Thorium finds use in incandescent gas mantles Gas mantel composition is 99% ThO_2 and 1% ceria. It also finds use in production of nuclear energy, X-ray targets, photoelectric cells. It is also used as an additive in alloys for making heating elements of 'sun lamps' for generating U.V rays. Thoria is a very good foundation for several catalysts is used as a dehydrating catalyst in certain organic reactions.

b) Uranium

Uranium is source of nuclear energy in nuclear reactors. It is used in coloring glass and pottery to give yellow or orange glazes. UO_2 is used in incandescent lamps. Uranium metal and uranium salts used in catalyst for the synthesis of ammonia by Haber's process.

c) Plutonium.

Pu^{239} is used as explosive ingredient in nuclear weapons. Used in the production of nuclear energy and for production of radioactive elements and higher transuranic elements like Am, Cm etc,.

1.4.viii).Model questions.

1. Why sharp bands are obtained in the absorption spectra of lanthanides and actinides?
2. More sharp bands are obtained in actinides than in lanthanides, What is the reason?
3. Write the colors of Ln^{+3} ions and An^{3+}.
4. Compare the lanthanides with actinides.
5. Write the equation for the calculation of magnetic moment and magnetic susceptibility.
6. Discuss the magnetic properties of lanthanides.
7. Why the calculated and observed values of μ are not coinciding? Explain.
8. Discuss the applications of lanthanides and actinides.

Recommended Books.

1.	G.Raj	Advanced inorganic chemistry.
2.	J.D.Lee	Concise inorganic chemistry.
3.	J.E.Huhey.	Inorganic chemistry.

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